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A Review of Standards of Performance for New Stationary Sources-Sulfuric Acid Plants

MITRE Corp, McLean, VA

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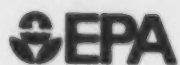
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by

Marvin Drabkin and Kathryn J. Brooks

Metrek Division of the MITRE Corporation
1820 Dolley Madison Boulevard
McLean, Virginia 22102

Contract No.68-02-2526

EPA Project Officer: Thomas Bibb

Emission Standards and Engineering Division

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1.0 EXECUTIVE SUMMARY

The objective of this report is to review the New Source Performance Standard (NSPS) for the sulfuric acid plant production unit in terms of developments in control technology, economics and new issues that have evolved since the original standard was promulgated in 1971. Possible revisions to the standard are analyzed in the light of compliance test data available for plants built since the promulgation of the NSPS. The NSPS review includes the SO₂ emission and acid mist emission standards. The opacity standard, while included in the sulfuric acid plant NSPS, is not reviewed separately since it is directly related to the acid mist emission standard. The following paragraphs summarize the results and conclusions of the analysis, as well as recommendations for future action.

1.1 Best Demonstrated Control Technology

Sulfur dioxide and acid mist are present in the tail gas from the contact process sulfuric acid production unit. In modern four-stage converter contact process plants burning sulfur with approximately 8 percent SO₂ in the converter feed, and producing 98 percent acid, SO₂ and acid mist emissions are generated at the rate of 13 to 28 kg/Mg of 100 percent acid (26 to 56 lb/ton) and 0.2 to 2 kg/Mg of 100 percent acid (0.4 to 4 lb/ton), respectively. The dual absorption process is the best demonstrated control

technology* for SO₂ emissions from sulfuric acid plants, while the high efficiency acid mist eliminator is the best demonstrated control technology for acid mist emissions. These two emission control systems have become the systems of choice for sulfuric acid plants built or modified since the promulation of the NSPS. Twenty-eight of the 32 new or modified sulfuric acid production plants built since 1971 and subject to NSPS incorporate the dual absorption process; and all 32 plants use the high efficiency acid mist eliminator.

1.2 Current SO₂ NSPS Levels Achievable With Best Demonstrated Control Technology

All 32 sulfuric acid production units subject to NSPS showed compliance with the current SO₂ NSPS control level of 2 kg/Mg (4 lb/ton). The 26 compliance test results for dual absorption plants showed a considerable range from a low of 0.16 kg/Mg (0.32 lb/ton) to a high of 1.9 kg/Mg (3.7 lb/ton) with an average of 0.09 kg/Mg (1.8 lb/ton). The average SO₂ emission level obtained in the NSPS compliance tests for dual absorption plants is about one order of magnitude lower than the SO₂ emission level obtained from uncontrolled single absorption plants. Information received on the performance of several sulfuric acid plants indicates that low SO₂ emission

*It should be noted that standards of performance for new sources established under Section 111 of the Clean Air Act reflect emission limits achievable with the best adequately demonstrated technological system of continuous emission reduction (taking into consideration the cost of achieving such emission reduction, as well as any nonair quality health and environmental impacts and energy requirements).

results achieved in NSPS compliance tests apparently do not reflect day-to-day SO₂ emission levels. These levels appear to rise toward the standard as the conversion catalyst ages and its activity drops. Additionally, there may be some question about the validity of low SO₂ NSPS values, i.e. less than 1 kg/Mg (2 lb/ton), due to defects in the original EPA Method 8. Based on all of these considerations, it is recommended that the level of SO₂ emissions as specified in the current NSPS not be changed at this time.

1.3 Economic Considerations Affecting the SO₂ NSPS

The cost of more frequent conversion catalyst replacement as a method of maintaining low SO₂ emission values, i.e., below 1 kg/Mg (2 lb/ton), was estimated in this study. Complete replacement of catalyst in the first three beds of the four-bed catalytic converter, approximately three times as frequently as is normally practiced, was estimated to result in an increase in operating cost of 55 cents/Mg of 100 percent acid. From an economic standpoint, this method would not be feasible since pretax profits could be reduced by 20 percent or more.

Based on an estimated sulfuric acid plant growth rate of four new production lines per year between 1981 and 1984, a 50 percent reduction of the present SO₂ NSPS level--from 2 kg/Mg (4 lb/ton) to 1 kg/Mg (2 lb/ton)--would result in a drop in the estimated percentage SO₂ contribution of these new sulfuric acid plants to the total national SO₂ emissions, from 0.04 percent to 0.02 percent. The national impact of a more stringent SO₂ NSPS would be marginal due

to the very small decrease in SO₂ emissions (resulting from a tighter standard) from the sulfuric acid plants projected to be built during the 1981 through 1984 period.

1.4 Current Acid Mist Levels (and Related Opacity Levels)
Achievable With Best Demonstrated Control Technology

All 32 sulfuric acid production units subject to NSPS showed compliance with the current acid mist NSPS control level of 0.075 kg/Mg of 100 percent acid (0.15 lb/ton). The NSPS compliance test data are all from plants with acid mist emission control provided by the high efficiency acid mist eliminator. The data showed a wide range with a low of 0.008 kg/Mg (0.016 lb//ton) to a high of 0.071 kg/Mg (0.141 lb/ton), and an overall average value of 0.04 kg/Mg (0.081 lb/ton). Acid mist emission (and related opacity) levels are unaffected by factors affecting SO₂ emissions, i.e., conversion catalyst aging. Rather, acid mist emissions are primarily a function of moisture levels in the sulfur feedstock and air fed to the sulfur burner, and the efficiency of final absorber operation. The order-of-magnitude spread observed in NSPS compliance test values is probably a result of variation in these factors. Additionally, variability in the original EPA Method 8 may have contributed to this spread. Making the acid mist standard more stringent is not believed to be practicable at this time because of the need to provide a margin of safety due to in-plant operating fluctuations, which introduce variable quantities of moisture into the sulfuric acid production line.

2.0 INTRODUCTION

In Section 111 of the Clean Air Act, "Standards of Performance for New Stationary Sources," a provision is set forth which requires that "The Administrator shall, at least every four years, review and, if appropriate, revise such standards following the procedure required by this subsection for promulgation of such standards." Pursuant to this requirement, the MITRE Corporation, under EPA Contract No. 68-02-2526, is to review 10 of the promulgated NSPS including the sulfuric acid plant production unit.

The main purpose of this report is to review the current sulfuric acid standards for SO₂, acid mist and opacity and to assess the need for revision on the basis of developments that have occurred or are expected to occur in the near future. This report addresses the following issues:

1. A review of the definition of the present standards and the NSPS monitoring requirements.
2. A discussion of the status of the sulfuric acid industry and the status of applicable control technology.
3. An analysis of SO₂, acid mist and opacity test results and review of level of performance of best demonstrated control technology for emission control.
4. A review of the impact of NSPS revision on sulfuric acid production economics, and the effect of new sulfuric acid plant construction on the NSPS.

Based on the information contained in this report, conclusions are presented and specific recommendations are made with respect to changes in the NSPS.

3.0 CURRENT STANDARDS FOR SULFURIC ACID PLANTS

3.1 Background Information

Prior to the promulgation of the NSPS in 1971, almost all existing contact process sulfuric acid plants were of the single-absorption design and had no SO₂ emission controls. Emissions from these plants ranged from 1500 to 6000 ppm SO₂ by volume, or from 10.8 kg of SO₂/Mg of 100 percent acid produced (21.5 lb/ton) to 42.5 kg of SO₂/Mg of 100 percent acid produced (85 lb/ton). Several state and local agencies limited SO₂ emissions to 500 ppm from new sulfuric acid plants, but few such facilities had been put into operation (EPA, 1971).

Many sulfuric acid plants utilized some type of acid mist control prior to 1971, but several had no controls whatsoever. Uncontrolled acid mist emissions varied between 2 and 50 mg/scf, or from 0.4 to 9 lb of H₂SO₄/ton of 100 percent acid produced, the lower figure representing emissions from a plant burning high-purity sulfur. State and local regulatory agencies had only begun to limit acid mist emissions to more stringent levels; i.e., some agencies had adopted limits of 1 and 2 mg/scf, respectively, for new and existing plants (EPA, 1971).

It is estimated that SO₂ emissions from sulfuric acid plants totalled 528,000 Mg (580,000 tons) in 1971 and 245,000 Mg (269,000 tons) in 1976 (Mann, 1978). This represents a 54 percent drop in SO₂ emissions from this industry in the first 5 years after the

promulgation of the NSPS for this pollutant.* By 1976 sulfuric acid plants, in compliance with the NSPS, represented 31 percent of the sulfuric acid industry capacity (Stanford Research Institute, 1977).

No corresponding data are available for the effect of the NSPS on total acid mist emissions from the industry.

3.2 Facilities Affected

The NSPS regulates sulfuric acid plants that were planned or under construction or modification as of August 17, 1971. Each sulfuric acid production unit (or "train") is the affected facility. The standards of performance apply to contact-process sulfuric acid and oleum facilities that burn elemental sulfur, alkylation acid, hydrogen sulfide, metallic sulfides, organic sulfides, mercaptans or acid sludge. The NSPS does not apply to metallurgical plants that use acid plants as control systems, or to chamber process plants or acid concentrators.

An existing sulfuric acid plant is subject to the promulgated NSPS if: (1) a physical or operational change in an existing facility causes an increase in the emission rate to the atmosphere of any pollutant to which the standard applies, or (2) if in the course of reconstruction of the facility, the fixed capital cost of the new components exceeds 50 percent of the fixed capital cost that would be required to construct a comparable entire new facility that meets the NSPS.

*It is not known what portion of this drop in SO₂ emissions is due to NSPS-controlled plants or to existing plants covered by State Implementation Plans (SIP).

3.3 Controlled Pollutants and Emission Levels

The pollutants to be controlled at sulfuric acid plants by the NSPS are defined by 40 CFR 60, Subpart H (as originally promulgated in 36 FR 24881 with subsequent modifications in 39 FR 20794) as follows:

1. Standard for sulfur dioxide

(a) "On and after the date. . . no owner or operator subject to the provisions of this subpart shall cause to be discharged into the atmosphere from any affected facility any gases which contain sulfur dioxide in excess of 2 kg per metric ton of acid produced (4 lb per ton), the production being expressed as 100 percent H_2SO_4 ."

2. Standard for acid mist

(a) "On and after the date. . . no owner or operator subject to the provisions of this subpart shall cause to be discharged into the atmosphere from any affected facility any gases which:

(1) Contain acid mist, expressed as H_2SO_4 , in excess of 0.075 kg per metric ton of acid produced (0.15 lb per ton), the production being expressed as 100 percent H_2SO_4 .

(2) Exhibit 10 percent opacity, or greater. Where the presence of uncombined water is the only reason for failure to meet the requirements of this paragraph, such failure will not be a violation of this section."

The values of these standards were derived from the following data sources:

1. A literature search revealed that over 20 dual-absorption plants had been operating successfully in Europe for several years using both elemental sulfur and roaster gas as feed and that three of these plants produced maximum SO_2 emissions ranging from 91 to 260 ppm SO_2 by volume, or from 0.6 kg of SO_2 per Mg of acid produced (1.2 lb/ton) to 1.6 kg of SO_2 per Mg of acid produced (3.1 lb/ton).

2. The two plants tested and evaluated by EPA engineers were a plant of typical dual-absorption design and a single-absorption spent-acid burning plant that used a sodium sulfite-bisulfite scrubbing process to recover SO_2 from tail gas.

The dual-absorption sulfuric acid plant was the first of its kind in the U.S. and was used by EPA as part of the best demonstrated control technology rationale for the NSPS for SO_2 emissions. Since 1971, 17 dual-absorption plants have been built in the U.S. with a total of 32 individual sulfuric acid units (or trains). This process has become the best demonstrated control technology for SO_2 control in the industry. No new sodium sulfite-bisulfite scrubbing units for SO_2 abatement have been installed on sulfuric acid plants built in the U.S.

Emission tests from both the original dual-absorption sulfuric acid plant and the single absorption plant with sodium sulfite-sodium bisulfite scrubbing, indicated that both operations were capable of maintaining SO_2 and acid mist emissions below 2.0 kg/Mg (4 lb/ton) and 0.075 kg/Mg (0.15 lb/ton), respectively, at full load operations. Additionally, control of acid mist below 0.075 kg/Mg (0.15 lb/ton) at these plants, resulted in no visible emissions from the stack, i.e., opacity was below 10 percent. Continuous stack monitoring at these plants indicated that at full load, the plants could be consistently operated so that SO_2 emissions would be kept within the limits of the performance standard (EPA, 1971). In Section 5.0 of this report, NSPS emission test results for SO_2 and acid mist are presented for

all the new sulfuric acid units completed since the promulgation of the standard.

3.4 Testing and Monitoring Requirements

3.4.1 Testing Requirements

Performance tests to verify compliance with SO₂, acid mist and opacity standards for sulfuric acid plants must be conducted within 60 days after the plant has reached its full capacity production rate, but not later than 180 days after the initial start-up of the facility (40 CFR 60.8). The EPA reference methods to be used in connection with sulfuric acid plant testing include:

1. Method 8 for the concentrations of SO₂ and acid mist
2. Method 1 for sample and velocity traverses
3. Method 2 for velocity and volumetric flow rate
4. Method 3 for gas analysis.

For Method 8, each performance test consists of three separate runs each at least 60 minutes with a minimum sample volume of 1.15 dscm (40.6 dscf). The arithmetic mean of the three runs taken is the test result to which compliance with the standard applies (40 CFR 60.8).

The sulfuric acid production rate, expressed as Mg/hr of 100 percent H₂SO₄, is to be determined during each testing period by suitable methods and confirmed by a material balance over the production system. Sulfur dioxide and acid mist emissions in kg/Mg

of 100 percent H_2SO_4 are determined by dividing the emission rate in kg/hr by the hourly 100 percent acid production rate.

3.4.2 Monitoring Requirements

SO_2 emissions in the tail gas from sulfuric acid plants are required to be continuously monitored. Continuous SO_2 monitoring instrumentation should be able to: (1) provide a record of performance and (2) provide intelligence to plant operating personnel such that suitable corrections can be made when the system is shown to be out of adjustment. Plant operators are required to maintain the monitoring equipment in calibration and to furnish records of SO_2 excess emission values to the Administrator of EPA or to the responsible State agency.

Measurement principles used in the gas analysis instruments are:

1. Infrared absorption
2. Colorimetric titration of iodine
3. Selective permeation of SO_2 through a membrane
4. Flame photometric measurement
5. Chromatographic measurement
6. Ultraviolet absorption.

The ultraviolet absorption system and the iodine titration method have received widespread application for SO_2 measurement in sulfuric acid plants subject to NSPS (Calvin and Kodras, 1976).

The continuous monitoring system is calibrated using a gas mixture of known SO₂ concentration as a calibration standard. Performance evaluation of the monitoring system is conducted using the SO₂ portion of EPA Method 8.

Excess SO₂ emissions are required to be reported to EPA (or appropriate state regulatory agencies) for all 3-hour periods of such emissions (or the arithmetic average of three consecutive 1-hour periods). Periods of excess emission are considered to occur when the integrated (or arithmetic average) plant stack SO₂ emission exceeds the standard of 2 kg/Mg (4 lb/ton) of 100 percent H₂SO₄ produced.

4.0 STATUS OF CONTROL TECHNOLOGY

4.1 Status of Sulfuric Acid Manufacturing Industry Since the Promulgation of the NSPS

4.1.1 Geographic Distribution

In 1971 there were 167 contact process sulfuric acid and oleum plants in the U.S. By 1977 the number of plants had decreased to 150. Thirty-two sulfuric acid units subject to NSPS are included in these 150 plants. Table 4-1 provides a summary by EPA region of the number of units subject to NSPS and their design tonnage. Table 4-2 is a tabulation of the eight new units planned or under construction which will be coming on-line by 1980.

Figure 4-1 shows the geographical distribution of contact process sulfuric acid units completed since 1971. The heaviest concentration of new units is in Region IV (Southeast). The high concentration of sulfuric acid units constructed in Florida since 1971 can be explained by the presence of rich phosphate rock deposits. Eighty percent of the phosphate rock mined goes into the manufacture of phosphatic fertilizers, which is also the end use of 60 percent of the total U.S. sulfuric acid production (Bureau of Mines, 1975; 1978). Since most sulfuric acid is consumed near its point of manufacture, units with production dedicated for phosphate fertilizer manufacture will, usually, be located near phosphate rock deposits.

4.1.2 Production

U.S. production of sulfuric acid in 1977 totalled approximately 30.9 million Mg (34 million short tons), representing an average

TABLE 4-1
SUMMARY OF NEW SULFURIC ACID PLANT COMPLETIONS
SINCE THE PROMULGATION OF THE NSPS

EPA Region	Plant		
	Units In Production (1971-1977)	Design Capacity ^a (100% H ₂ SO ₄) Mg/day (TPD)	Percent of Total New Design Capacity
II	2	1,820 (2000)	4.6
IV	18	28,670 (31,500)	72.3
V	1	230 (250)	0.6
VI	4	5,370 (5900)	13.6
IX	1	1,640 (1800)	4.1
X	6	1,890 (2080)	4.8
Total	32	39,610 (43,530)	100.0
	Average	1200 (1300)	

^aThese units all use the double absorption process except one plant (one new unit and two existing units) in Region VI and one plant (two new units) in Region X which use a single absorption process with ammonia scrubbing. One new plant in Region V is currently retrofitting from single to double absorption.

TABLE 4-2

SULFURIC ACID PLANTS PLANNED OR UNDER CONSTRUCTION

Region	Company	Plant Location	No. of Units	Plant Capacity Mg/day (TPD)	Anticipated Startup Date	Source
III	Getty Oil	Delaware City, Del.	2	540 (600) ^a	1980	Hansen, 1978
IV	Occidental Chemical Co.	White Springs, Fla.	2	3640 (4000) ^b	Late 1979	Hansen, 1978
	Royster Co.	Mulberry, Fla.	1	720 (800)	Late 1979	Hansen, 1978
V	Shell Chemical Co. ^c	Wood River, Ill.	1	230 (250)	Fall, 1979	Williams, 1977
VI	American Cyanamid Co.	Fortier, La.	1	1460 (1600)	Fall, 1978	Chem. Eng., 1977
VII	U.S. Army Sunflower Arsenal	Lawrence, Kan.	1	270 (300)	1980	Hansen, 1978
		TOTAL	8	6860 (7500)		

^a 2 - 270 Mg/day (300 TPD) units.^b 2 - 1820 Mg/day (2000 TPD) units.^c Retrofit of dual absorption system.



FIGURE 4-1
CONTACT PROCESS SULFURIC ACID PLANTS
COMPLETED IN THE U.S. SINCE 1971

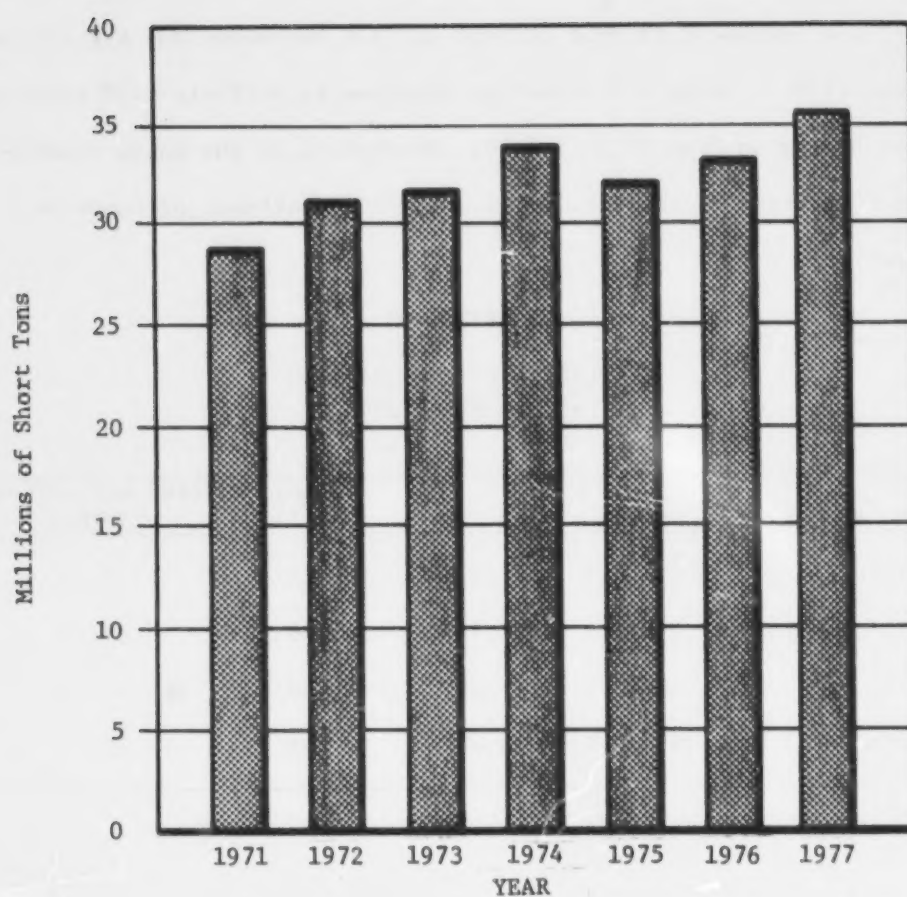
yearly increase of 1.9 percent (575,000 Mg) since 1971 (Department of Commerce, 1976; Chemical and Engineering News, 1978). Figure 4-2 shows total annual production of sulfuric acid for 1971 to 1977, including production by the lead chamber process, which has almost been phased out of the industry (EPA, 1976). Production by the contact process alone represented 99.3 percent of total production in 1971 and increased to 99.8 percent in 1976 (Chemical and Engineering News, 1978). Table 4-3 shows the increase in sulfuric acid production by region from 1975 to 1976. Production in the South represented 70 percent of the U.S. total in 1976 (Department of Commerce, 1976).

TABLE 4-3
SULFURIC ACID PRODUCTION
(Mg of 100% H₂SO₄)

Region	1975	1976	Change (%)	Total Production 1976(%)
Northeast	1,728.2	1,527.2	-12	5
North Central	2,804.4	2,636.9	-6	9
West	4,110.7	4,445.5	+8	16
South	19,640.9	20,667.9	+5	70

Source: Department of Commerce, 1976.

The growth of the sulfuric acid industry since the promulgation of the NSPS has been largely dominated by the growth in the phosphate fertilizer industry in the early and mid-seventies. Of the 32



SOURCE: Department of Commerce, 1976; 1977.

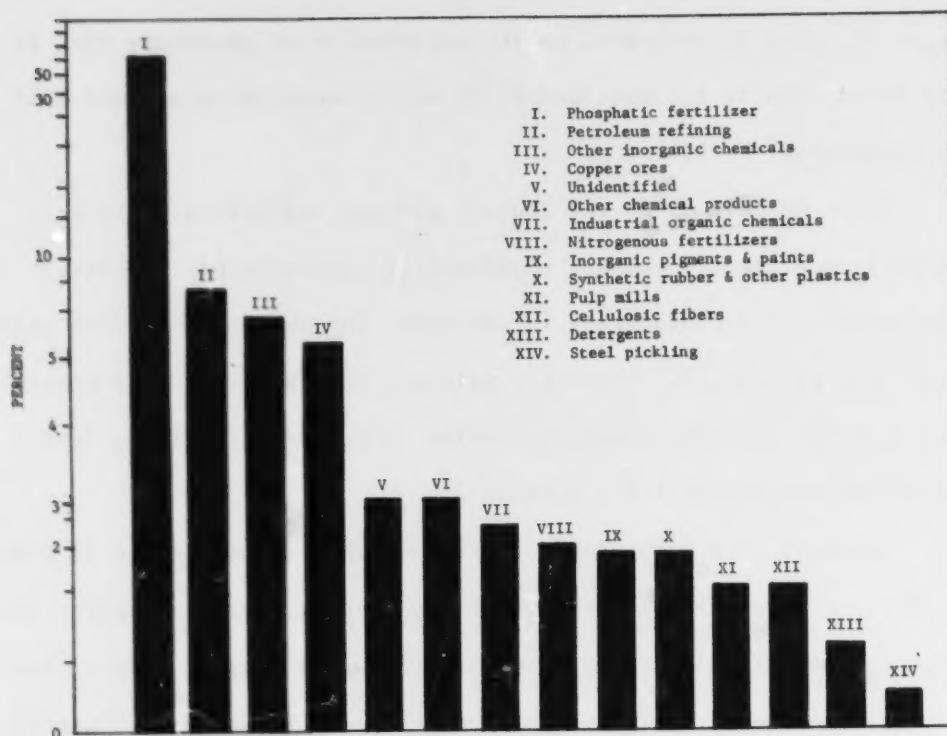
FIGURE 4-2
GROSS TOTAL PRODUCTION OF SULFURIC ACID:
1971 TO 1977

contact process sulfuric acid units subject to NSPS, the output of at least 24 units is dedicated to the acidulation of phosphate rock as the first step in the manufacture of wet process phosphate and acid superphosphate fertilizers.

About 68 percent of the contact process sulfuric acid is produced from elemental sulfur, representing approximately 85 percent of the total sulfur consumption in the U.S. The remaining acid is made from iron pyrites (4.5 percent); tail gas from smelters (9 percent); and hydrogen sulfide, spent alkylation acid, and acid sludge from petroleum refineries (18.5 percent).

Sulfuric acid is produced in various concentrations and in four grades: commercial, electrolyte or high purity, textile (having low organic content), and chemically pure (C.P.) or reagent grade. The various end uses of sulfuric acid are shown in Figure 4-3. In addition to the manufacturing of fertilizer, other major uses are petroleum refining (7 percent), other inorganic chemicals (6 percent), and copper ores (5 percent).

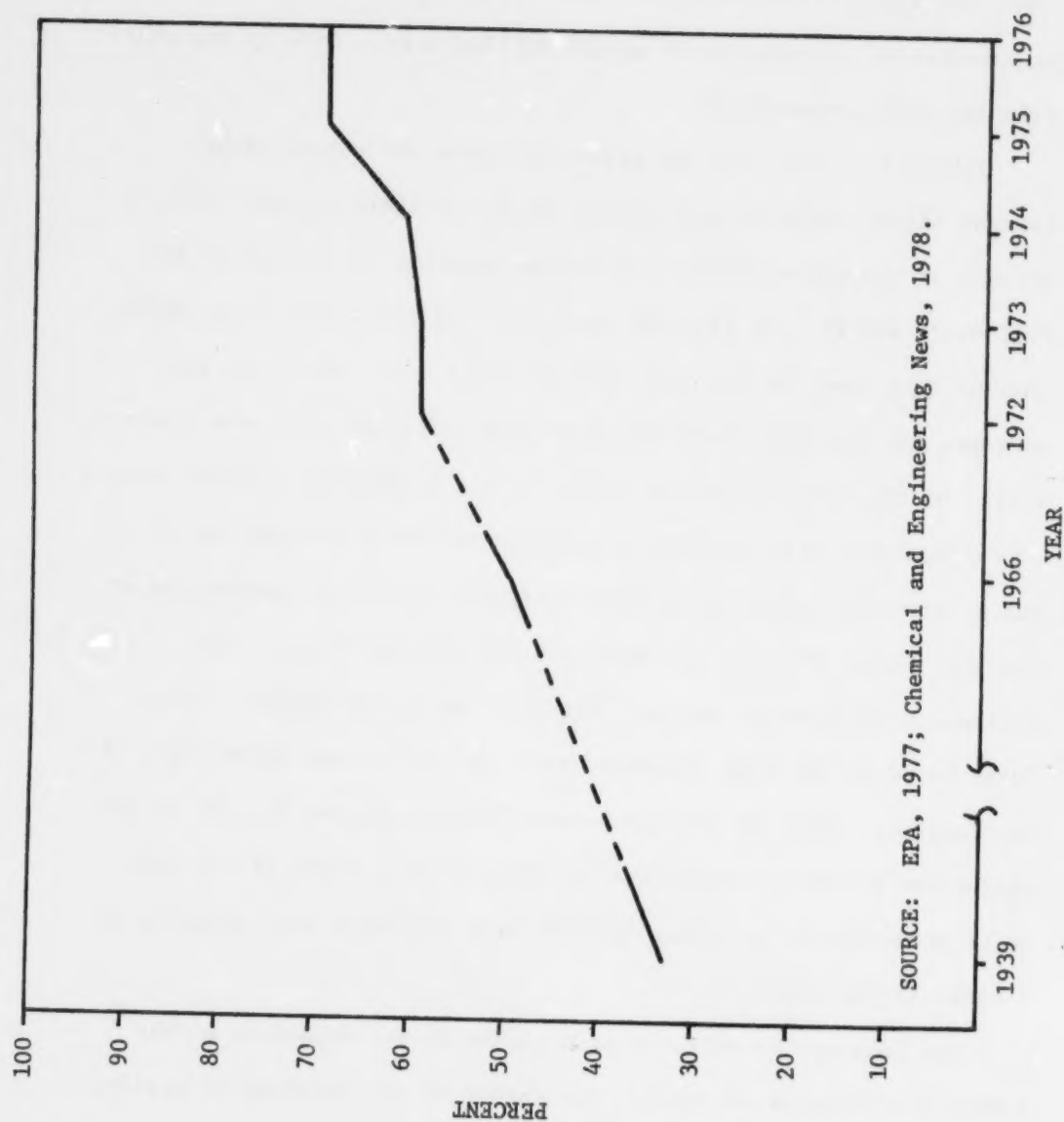
An increasing number of sulfuric acid consumers, specifically fertilizer manufacturers, produce their own sulfuric acid for captive use. The ratio of production for merchant sales (or shipments) to production for captive use decreased from 2:1 in 1939 and 1:1 in 1966 to 0.7:1 in 1973. This relationship is shown in Figure 4-4.



Note: Uses under IX are: uranium & vanadium ore, other ore, other paper products, drugs, pesticides, other agricultural chemicals, explosives, water treating compounds, rubber & miscellaneous plastic products, nonferrous metals, other primary metals, and storage batteries (acid). There were no sulfuric acid exports in 1977.

SOURCE: Bureau of Mines, 1978.

FIGURE 4-3
SULFURIC ACID END USES



SOURCE: EPA, 1977; Chemical and Engineering News, 1978.

FIGURE 4-4
PERCENT OF TOTAL PRODUCTION OF SULFURIC ACID IN
CAPTIVE USE

4.1.3 Industrial Trends

U.S. sulfuric acid production in 1968 was 25.9 million metric tons, and approximately 30.9 million metric tons in 1977. Production is expected to increase to 49 and 80 million metric tons by the years 1980 and 1990, respectively.

Tables 4-1, 4-2, 4-3 and Figure 4-1 show the strong trend towards siting sulfuric acid plants in the southern states. Over 86 percent of the new sulfuric acid design capacity is located in EPA Regions IV and VI. In 1971 EPA projected two new units to be coming on-line each year for the next several years (EPA, 1971). On the average, six new units have actually been completed each year since 1971. Of the total of 32 new units, 15 are located in Florida. Most of the sulfuric acid production units in the South are captive in nature with the output going into phosphate fertilizer production at the same plant complex. In 1976, over 70 percent of the total national production of new sulfuric acid was in the South. Therefore, based on the high phosphate rock concentrations (Department of the Interior, 1973) on the new construction in Region IV, and on the production trends of sulfuric acid (Figure 4-4), three of the four units projected to be coming on-line each year will most probably be located in the South.

The location of sulfuric acid plants is not dependent on the location of sources of sulfur, but rather on the location of various industries associated with the use of sulfuric acid, i.e. the

fertilizer and petroleum refining industries. The future supply of sulfur for new acid will lean more heavily on recovered sulfur from petroleum production and sulfur dioxide abatement and less on mined (Frasch) sulfur.

4.2 Contact Process for Sulfuric Acid Production

All contact sulfuric acid manufacturing processes incorporate three basic operations: (1) burning of sulfur or sulfur-bearing feedstocks to form SO_2 , (2) catalytic oxidation of SO_2 to SO_3 , and (3) absorption of SO_3 in a strong acid stream. The several variations in the process are due principally to differences in feedstocks. The least complicated systems are those that burn elemental sulfur. Where there are appreciable organics and moisture as in spent acid and acid sludge, additional operations are required to remove moisture and particulates prior to catalysis and absorption. The composition of feedstock can affect the sulfur conversion ratio, the volume of exhaust gases and the character and rate of pollutant releases.

4.2.1 Elemental Sulfur Burning Plants

Figure 4-5 is a schematic diagram of a contact sulfuric plant burning elemental sulfur. Sulfur is burned to form a gas mixture which is approximately 8 to 10 percent sulfur dioxide, 11 to 13 percent oxygen, and 79 percent nitrogen. Combustion air is predried by passing through a packed tower circulating 98 percent sulfuric acid. Air drying minimizes acid mist formation and resultant corrosion throughout the system.

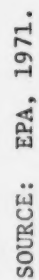


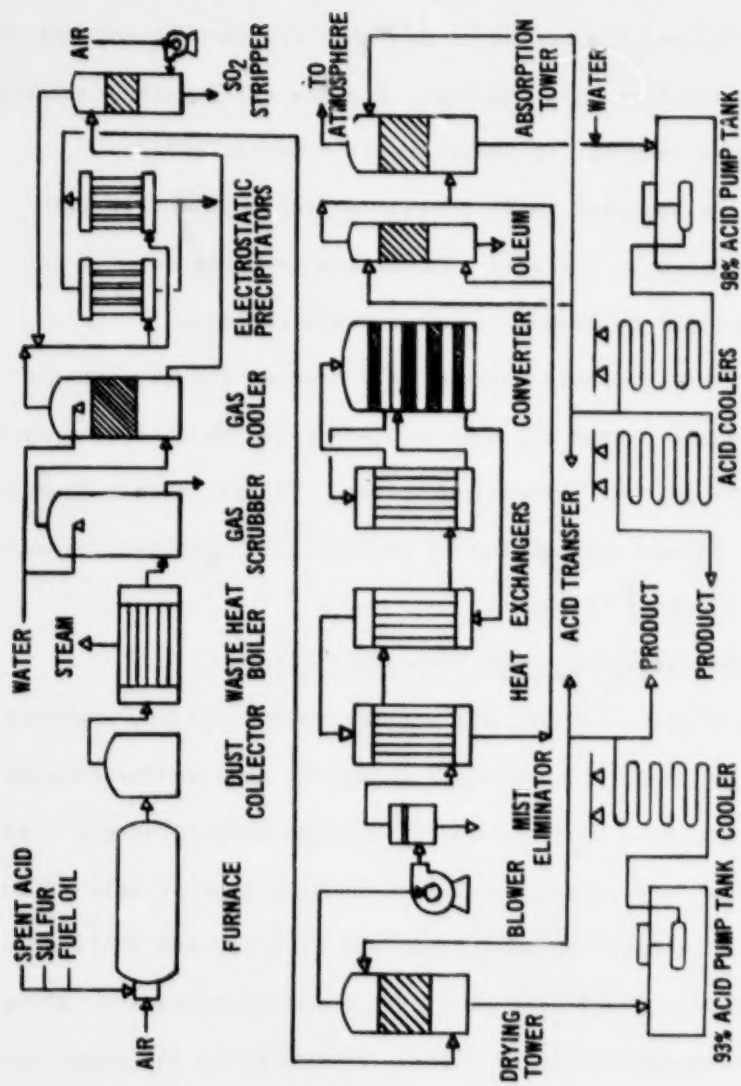
FIGURE 4-5
CONTACT-PROCESS SULFURIC ACID PLANT BURNING
ELEMENTAL SULFUR

SO_2 is oxidized to SO_3 in the presence of a catalyst containing approximately 5 percent vanadium pentoxide. The temperature of the reacting gas mixture increases as the composition approaches equilibrium. Maximum conversion to SO_3 requires several conversion stages with intermediate gas cooling. The gas exiting the converter is cooled in an economizer to temperatures between 230° and 260°C , and SO_3 is absorbed in 98 percent sulfuric acid circulating in a packed tower. The acid content and temperature must be carefully controlled to prevent excessive SO_3 release.

If fuming sulfuric acid (oleum) is produced, the SO_3 containing gases are first passed through an oleum tower which is fed with acid from the 98 percent absorption system. The gas stream from the oleum tower is passed through the 98 percent acid absorber for recovery of residual sulfur trioxide.

4.2.2 Spent Acid and Other By-Product Plants

Where spent acid, sludge, and similar feedstocks are employed, the processes are more elaborate and expensive than sulfur-burning plants due to the fact that the sulfur dioxide containing gas stream is contaminated. Gases must be cleaned if high-quality acid is to be produced. This requires additional gas cleaning and cooling equipment to remove dust, acid mist, and gaseous impurities, along with excessive amounts of water vapor. Purification equipment consists of cyclones, electrostatic dust and mist precipitators, plus scrubbers and gas-cooling towers in various combinations. Figure 4-6



SOURCE: EPA, 1971.

FIGURE 4-6
CONTACT-PROCESS SULFURIC ACID PLANT
BURNING SPENT ACID

shows one possible configuration of a spent acid plant. The balance of the process following the drying tower is essentially the same as an elemental sulfur-burning plant.

A few plants burning only hydrogen sulfide or hydrogen sulfide plus elemental sulfur use a simplified version of the above process. Wet gases from the combustion chamber and waste heat boiler are charged directly to the converter with no intermediate treatment. Gases from the converter flow to the absorber, through which 70 to 93 percent sulfuric acid is circulating. In such a "wet gas" plant much of the sulfur trioxide from the converter is in the form of acid mist which is not absorbed in the absorption tower. High efficiency mist collectors are utilized both to recover product and to prevent excessive air pollution.

4.3 Emissions from Contact Process Sulfuric Acid Plants

4.3.1 Sulfur Dioxide

Mass SO_2 emissions vary inversely as a function of the sulfur conversion efficiency (i.e., fraction of SO_2 oxidized to SO_3). For sulfur burning plants, the inlet SO_2 concentration to the catalytic converters normally ranges between 7.5 and 8.5 percent but can be as high as 10.5 percent. Conversion efficiency depends upon the number of stages in the catalytic converter and, to a lesser extent, on the amount of catalyst.

Most plants built prior to 1960 had only three catalyst stages, and overall conversion efficiencies were approximately 95 to 96

percent. Sulfur burning plants built since 1960 generally have four stages* and efficiencies normally range between 96 and 98 percent. For three-stage plants, SO₂ release ranges between 28 and 35 kg/Mg and for four-stage plants, between 13 and 28 kg/Mg.

Spent acid plants followed the same design trend. Most three-stage plants were built prior to 1960 and four-stage plants have usually been built after 1960. Typical SO₂ concentrations in the converter feed, conversion efficiencies, and resultant emissions for plants burning sulfur, H₂S or primarily acid sludge are given in Table 4-4.

TABLE 4-4
SULFUR DIOXIDE CONVERSION EFFICIENCIES AND EMISSIONS
FOR FOUR-STAGE CONVERTERS

Feedstock	Sulfur	Hydrogen Sulfide (with some other sulfur compounds)	Acid Sludge
SO ₂ in converter feed, % by volume	7.5 to 8.5	7	6 to 8
Sulfur conversion to SO ₃ , % by weight	96 to 98		
SO ₂ emissions, kg/Mg 100% acid	13 to 28	25 to 43	15 to 56
SO ₂ emissions, ppm by volume	1500 to 4000	1500 to 4000	1500 to 4000

Source: EPA, 1971.

*There have been a number of five-stage converters included in dual absorption plants built since 1971 (see Section 5.2.1).

Exit SO₂ concentrations from contact plants vary as a function of the SO₂ content of dry gases fed to the converter. Where SO₂ strength is relatively low, there is a significantly greater volume of gases handled per ton of acid produced.

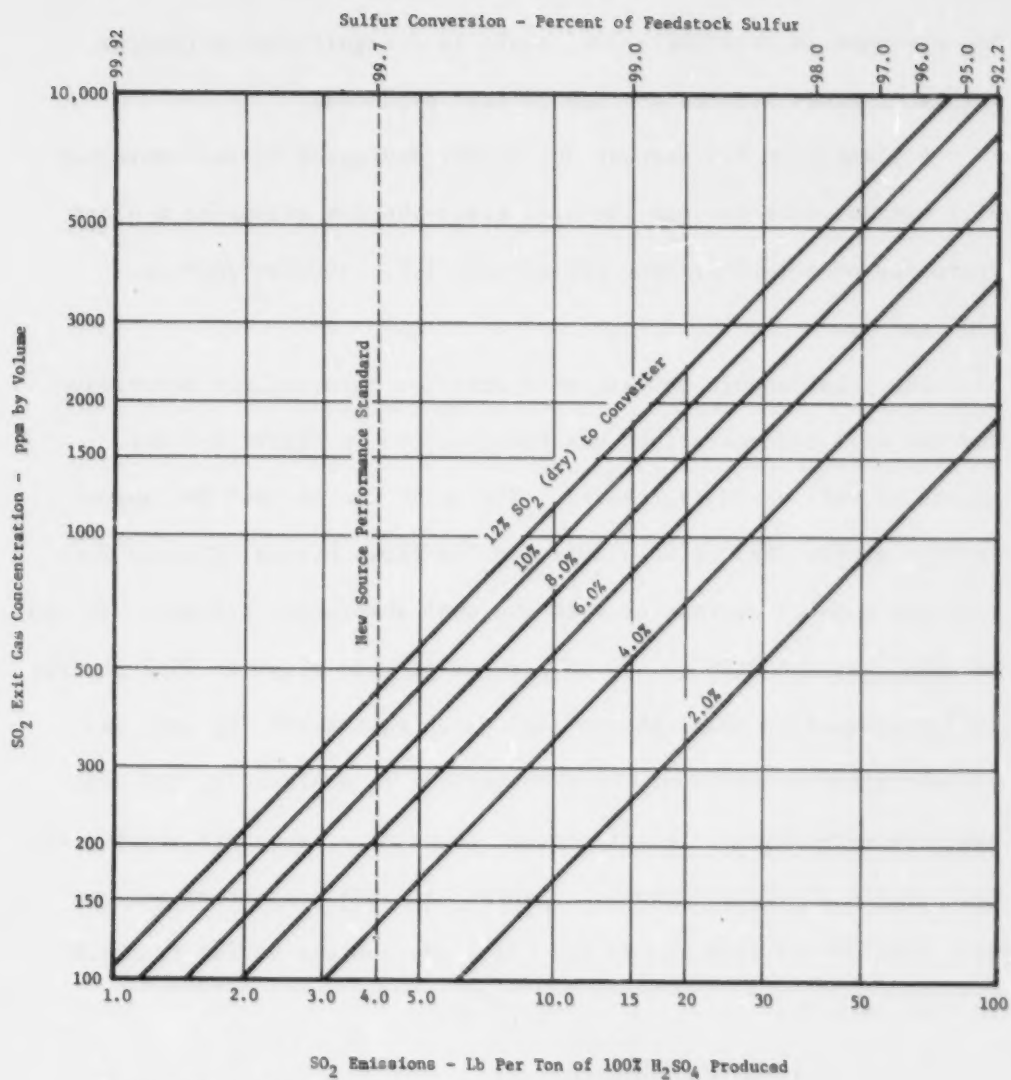
A plant with 4.0 percent SO₂ in the dry gases to the converter will exhaust over two and one-half times the gas volume of a plant operating on a 10.0 percent SO₂ stream, i.e., 4600 sm³/Mg* vs. 1700 sm³/Mg.

The relationship between mass emission rate, sulfur conversion and SO₂ exit concentrations has been plotted in Figure 4-7 for plants of various SO₂ strengths. The curve can be used for uncontrolled single absorption plants and for those plants equipped with tail gas removal systems or with the dual absorption process. It can be seen that the NSPS of 4.0 lb per ton of acid requires 99.7 percent sulfur conversion (dual absorption) or an equivalent SO₂ exit gas concentration of 380 ppm. This conversion is achieved by the dual absorption technique. At 98 percent conversion, which is optimum for most single absorption contact plants, exit SO₂ concentrations can vary from 900 to 2500 ppm as the inlet SO₂ content varies from 4.0 to 10.0 percent.

4.3.2 Acid Mist Formation

The sulfuric acid liquid loading in the tail gas from the absorber in a contact process plant is classified into two broad areas based on the acid particle size: (1) spray, which is defined

*Standard cubic meter per metric ton.



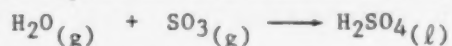
Source: EPA, 1976

FIGURE 4-7
SULFURIC ACID PLANT FEEDSTOCK SULFUR CONVERSION
VS. VOLUMETRIC AND MASS SO_2 EMISSIONS AT VARIOUS
INLET SO_2 CONCENTRATIONS BY VOLUME

as acid particles larger than 10 microns, and (2) mist, which is defined as acid particles smaller than 10 microns (Duros and Kennedy, 1978).*

Spray is primarily formed by mechanical generation of particles that are formed when a gas and liquid are mixed together. Examples of spray formation are liquid droplets formed by nozzles and liquid entrainment leaving a packed tower. A typical tower design in a modern acid plant will have a spray loading of 175 to 350 milligrams per actual cubic meter (mg/AM³) under normal operating conditions.

Acid mist formation is more complex to define than spray. There are two primary mechanisms of acid mist formation. The first mechanism is the reaction between two vapors forming a liquid or solid (i.e., change of state where volume reactants is much greater than volume products). This is best exemplified by the reaction of sulfur trioxide and water vapors to form submicronic sulfuric acid mist.



The second mechanism of mist formation is vapor condensation in the bulk gas phase by lowering the gas stream temperature beyond the liquid dew point. The dew point of a sulfuric acid under typical conditions is about 300° to 350°F. However, because of the uncertainties of bulk phase temperature differences, nonideal conditions and wall effects, the gas stream temperature is normally maintained between 375° to 425°F. This is done to insure that acid mist is not present to attack metal equipment.

*The EPA definition of acid mist (Method 8) includes both liquid sulfuric acid particles and SO₃ gas.

The formation of sulfuric acid mist in an acid plant is due to a combination of these mechanisms. When a gas stream containing SO_3 , H_2SO_4 and H_2O vapor is cooled below the liquid dew point, the H_2SO_4 vapor condenses and the SO_3 vapor and H_2O vapor combine to form H_2SO_4 , which also condenses. Submicronic mist particles will be formed when the gas is cooled faster than the condensable vapor can be removed by mass transfer (i.e., "shock cooling"). The conditions for "shock cooling" are present in the absorbing towers of an acid plant.

The practical key to controlling mist formation is to keep the H_2O content in a gas stream as low as possible. As an example of mist forming capability of extraneous water, 1 mg of water vapor carried through the plant has the potential to produce 190 mg/m^3 of submicronic acid mist (Duros and Kennedy, 1978). The water content of the gas stream can be increased by:

1. High organic content of contaminated elemental sulfur (sulfur burning plants only),
2. Acid mist carryover from upstream equipment,
3. Inadequate drying of the process air stream, and
4. Low absorbing tower acid strengths

At acid strengths below 98.5 percent, the acid begins to exert a measurable water vapor pressure. The optimum absorbing tower acid has the minimum vapor pressure of both water (minimizing mist formation problems) and sulfur trioxide (minimizing SO_3 slippage).

In oleum producing plants, greater quantities and a much finer mist are produced. From 85 to 95 weight percent of the particles are less than 2 microns in diameter as compared with about 30 percent less than 2 microns for 98 percent acid production. Acid mist emissions prior to control equipment range between 0.2 to 2 kg/Mg for sulfur burning contact plants producing no oleum to about 0.5 to 5 kg/Mg for spent acid burning plants producing oleum, based on an 8 percent SO_2 feed to the converter.

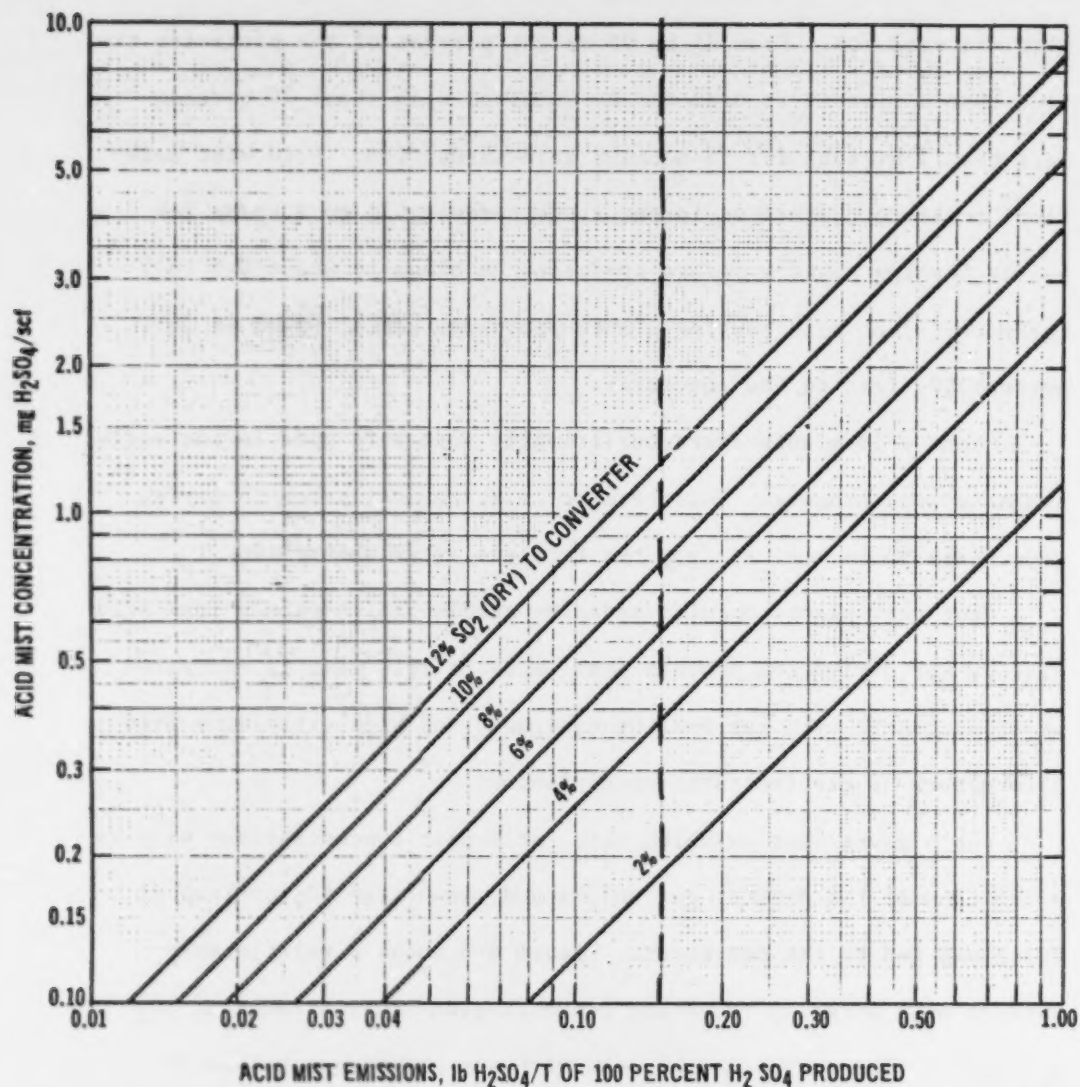
Spent acid plants characteristically form acid mist in the early stages of the process. This requires mist removal prior to drying and oxidation as well as from the tail gas after absorption.

"Wet gas" plants burning hydrogen sulfide deliberately form acid mist by not drying the process gas. Much of this mist is recovered as product acid with gas cooling equipment and high efficiency mist eliminators or electrostatic precipitators.

For a given mass emission rate, acid mist concentrations vary as a function of the exhaust gas volume and, thus, the SO_2 control of the gases fed to the converter. Figure 4-8 shows a relationship between mass emission rates and concentrations over a range of SO_2 strengths. The curves can be used with any gas stream before or after mist eliminators, provided there is no dilution.

4.3.3 Visible Emissions (Opacity)

Acid mist in exhaust gases creates visible emissions ranging from white to blue depending on particle size, concentration and



SOURCE: EPA, 1977.

FIGURE 4-8
SULFURIC ACID PLANT CONCENTRATIONS OF MIST
FOR MASS STACK EMISSIONS PER UNIT OF
PRODUCTION AT INLET SO_2 VOLUME CONCENTRATIONS

background. Where there is no control of mist, opacities generally range from 80 to 100 percent.

The effect of acid mist on opacity is more dependent on the size of the mist particle than on the quantity of mist. The smaller particles scatter light more, producing a denser plume. Nevertheless, it has been demonstrated that opacity of the plume from an efficient SO_3 absorber is a function of acid mist concentration and that visible emissions can be eliminated by minimizing acid mist levels in the acid plant tail gas, through the use of a good mist eliminator. At the current NSPS acid mist control level, there are essentially no visible emissions.

4.3.4 Oxides of Nitrogen

Nitrogen oxides present in the converter gas also cause acid mist emissions, since they reduce the efficiency of the absorption tower. Nitrogen oxides may result from the fixation of atmospheric nitrogen in high temperature sulfur furnaces, or may be formed from nitrogen compounds in the feedstocks. Nitrogen oxides can be held to a reasonable minimum by using the same techniques which have been applied to steam generators. For instance, in the decomposition of spent acid containing nitrogen compounds, operation at furnace temperatures less than about 2000°F and a low oxygen content will generally keep nitrogen oxides concentrations below 100 ppm.

4.4 Control Technology Applicable to the NSPS Control of SO₂ Emissions from Contact Process Sulfuric Acid Plants

There are a few physical mechanisms and many chemical means of removing SO₂ from gas streams. Almost any soluble alkaline material will absorb a significant fraction of SO₂ even in a crude scrubber. For years, sulfur dioxide has been removed from many process gases where the SO₂ adversely affected the product. The problems of removing SO₂ from acid plant gases are principally that of finding the least expensive mechanism consistent with minimal formation of undesirable by-products. The control processes in use by the sulfuric acid industry (in those units installed since the promulgation of the NSPS), are reviewed below.

4.4.1 Dual Absorption Process

The dual absorption process (used partially as the basis of the rationale for the SO₂ NSPS) has become the SO₂ control system of choice by the sulfuric acid industry since the promulgation of the NSPS. This can be seen by examination of Table 4-5, which presents a tabulation of the new sulfuric acid units built since the promulgation of the NSPS together with their locations, design capacities, basic process design, and SO₂ and acid mist control technologies. Out of 32 new units built since the promulgation of the NSPS, 28 have employed the dual absorption process for SO₂ control. This process offers the following advantages over other SO₂ control processes:

- As opposed to single absorption with scrubbing, a greater fraction of the sulfur in the feed is converted to sulfuric acid.

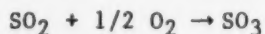
TABLE 4-5
CONTACT PROCESS SULFURIC ACID PLANTS SINCE PROMULGATION OF THE SDQS

EPA Region	Company	State and Locality	Year Completed	No. of Units	Plant Design Capacity (lb/day (TPD))	Process Design		Emissions Control System		Reference
						Single Absorption	Double Absorption	SO ₂	Acid Mist	
II	HL Industries, Inc.	Bayville, New Jersey	1973	2	3,810 (2,000)		x	Process	Mist Eliminator	CDM, 1978
IV	Cardinal, Inc.	Flordia	1978	1	2,370 (2,400)		x ^b	Process	Fiber Mist Eliminator	CDM, 1978
	Agri-Chem, Inc.	Tempe, Arizona	1975	2	3,800		x ^b	Process	Fiber Mist Eliminator	CDM, 1978
	CF Chemicals, Inc.	Benton, Missouri	1975	1	3,280 (2,000)		x	Process	Brink Fiber Mist Eliminator	CDM, 1978
	CF Chemicals, Inc.	Plant City, Florida	1974	2	2,910 (3,200)		x	Process	Brink Fiber Mist Eliminator	CDM, 1978
	W. R. Grace & Co.	Benton, Missouri	1976, 1977	3	4,370 (4,800)		x	Process	Brink Fiber Mist Eliminator	CDM, 1978
	International Minerals & Chemical Corp.	New Haven, Connecticut	1975	3	5,460 (6,000)		x	Process	Brink Fiber Mist Eliminator	CDM, 1978
	Oxidation Partners Corp.	White Springs, Georgia	1975	2	3,280 (3,600)		x ^b	Process	Parson-Turner Dual-Stage Mist Eliminator	CDM, 1978
	American Cyanamid Co.	Sevenson, Maryland	1975	1	720 (800)		x	Process	Mist Eliminator	PDGCo., 1977
	Mississippi Chemical Corp.	Marshall, Mississippi	1975	1	1,370 (1,500)		x	Process	Boyer/Lurgi Mist Eliminator	CDM, 1978
	Texas Gulf, Inc.	McGregor, Texas	1975	2	2,740 (3,000)		x	Process	Brink Fiber Mist Eliminator	CDM, 1978
V	Anlin Chemical Corp. ^a	Alton, Illinois	1974	1	230 (250)	x		Molecular Sieves	Fiber Mist Eliminator	Williams, 1977
VI	Agri-Chem. Co.	Louisiana	1974	2	3,090 (3,600)		x ^b	Process	York "M" 2 Stage Mist Eliminator	Speziall, 1978
	Fresport Chem. Co.	Uncle Sam, Texas	1974	1	1,440 (1,600)		x	Process	Fiber Mist Eliminator	Speziall, 1978
IX	Bohn & Haas	Dear Park, California		1	640 (700)	x		Ammonia Scrubbing	Fiber Mist Eliminator	Speziall, 1978
	Valley Nitrogen Prod., Inc.	Bellevue, Washington	1975	1	1,640 (1,800)		x ^b	Process	Brink Fiber Mist Eliminator	Raynolds, 1977
X	Meeker Industries	Idaho	1974	1	770 (850)		x	Process	Brink Fiber Mist Eliminator	Pfander, 1978
	J. R. Sampson Co.	Pocatello, Idaho	1976	2	820 (900)		x	Process	Brink Fiber Mist Eliminator	Pfander, 1978
	Allied Chem. Corp.	Washington		3	300 (330)		x ^c	Process	Fiber Mist Eliminator	Hooper, 1978
TOTALS					99,810 (43,330)					
AVERAGE					1,740 (1,767)					

^aThis facility was purchased by Shell Oil Co. in 1976; the plant is being modified to incorporate a double absorption process for SO₂ control.
^bThese units are of Ferrous design, incorporating a 3-bud converter rather than the usual 4-bud converter.
^cOne of these units is of Ferrous design (note 5).
 Source: MINE Corp., 1978; PDGCo., Inc., 1977.

- There are no by-products.
- Contact acid plant operators are familiar with the operations involved.

Figure 4-9 is a process flowsheet of the dual absorption process. The SO_3 formed in the first three converter stages is removed in a primary absorption tower and the remainder of the gas is returned to the final conversion stage(s). Removal of a product of a reversible reaction

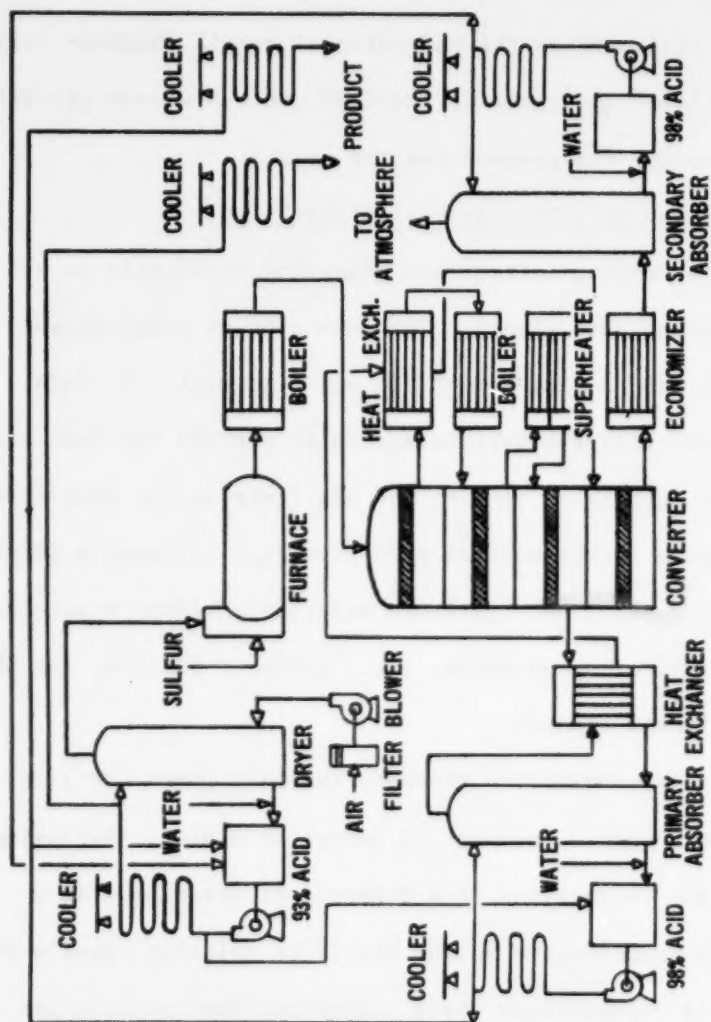


drives the oxidation further toward completion approaching the reaction equilibrium expressed by:

$$K = \frac{(\text{SO}_3)}{(\text{SO}_2) (\text{O}_2)^{1/2}}$$

where K is the reaction equilibrium constant peculiar to the temperature of the reaction and the parenthetical entities are the molar quantities of the gases involved. The resulting SO_3 is absorbed in a secondary absorption tower obtaining at least 99.7 percent overall conversion of the sulfur to sulfuric acid.

The dual absorption process permits higher inlet SO_2 concentrations than normally used in single absorption plants since the second conversion step effectively handles the residual SO_2 from the first conversion step. Higher inlet SO_2 concentrations permit a reduction in equipment size which partially offset the cost of the additional equipment required for a dual absorption plant. The dual absorption equipment occupies little more space than a conventional plant, even though an additional absorber is required.



SOURCE: EPA, 1971.

FIGURE 4-9
DUAL ABSORPTION SULFURIC ACID PLANT
FLOW DIAGRAM

Spent acid or H_2S may be used as feedstock in a dual absorption process with appropriate conventional process gas pretreatment, i.e., particulate removal. The dual absorption process requires the same types of equipment as the conventional single absorber design. Although additional equipment is required, the on-stream production factor and manpower requirement are the same.

4.4.2 Sodium Sulfite - Bisulfite Scrubbing

Tail gas scrubbing systems are generally applicable to all classes of contact acid plants. They can provide simultaneous control of SO_2 and to some extent SO_3 and acid mist. To date only the sodium sulfite-bisulfite scrubbing process has been demonstrated to be capable of meeting the SO_2 limit in the most cost effective manner. Other control processes such as ammonia scrubbing can meet the standard, but costs are relatively highly dependent on the marketability of by-products, i.e., ammonium sulfate, for which there may be little demand.

In the Wellman-Power Gas process, the tail gases are first passed through a mist eliminator to reduce acid mist. Following mist removal, the SO_2 is absorbed in a three-stage absorber with a sodium sulfite solution. A sodium bisulfite solution results and is fed to a heated crystallizer where sodium sulfite crystals are formed and SO_2 gas and water vapor are released. The crystals are separated from the mother liquor and dissolved in the recovered condensate for recycle to the absorber. The recovered wet SO_2 is sent back to the acid plant.

In all processes employing sulfite-bisulfite absorption even without regeneration, some portion of the sulfite is oxidized to sulfate, from which the sulfur dioxide cannot be regenerated in the heating sequence. This sulfate must be purged from the system. In the Wellman-Power Gas process, some thiosulfate is also formed. Apparently the extent of oxidation is dependent on several factors such as the oxygen content of the gas stream, the temperature and residence time of the liquor in the recovery sections, and the presence of contaminants that may act as oxidation catalysts. Despite the effectiveness of the sodium sulfite-bisulfite scrubbing process, none of the sulfuric acid plants installed since the promulgation of the NSPS have employed this process for tail gas SO₂ control.

4.4.3 Ammonia Scrubbing

The ammonia scrubbing process uses anhydrous ammonia (NH₃) and water make-up in a two-stage scrubbing system to remove SO₂ from acid plant tail gas. Excess ammonium sulfite-bisulfite solution is reacted with sulfuric acid in a stripper to evolve SO₂ gas and produce an ammonium sulfate byproduct solution. The SO₂ is returned to the acid plant while the solution is treated for the production of fertilizer grade ammonium sulfate. The process is dependent on a suitable market for ammonium sulfate.

Since the promulgation of the NSPS for sulfuric acid plants, one new plant (two units) and a new unit added to an existing plant, are employing an ammonia scrubbing system for tail gas SO₂ emissions control.

4.4.4 Molecular Sieves

This process utilizes a proprietary molecular sieve system in which SO_2 is adsorbed on synthetic zeolites. The adsorbed material is desorbed by purified hot tail gas from the operating system and sent back to the acid plant.

Since the promulgation of the sulfuric acid plant NSPS, one new unit has incorporated a molecular sieve system for SO_2 control in the original design. However, extensive operational difficulties with this system have caused this plant to be retrofitted with a dual absorption system for SO_2 control.

4.5 Control Technology Applicable to the NSPS for Acid Mist Emissions from Contact Process Sulfuric Acid Plants

Effective control of stack gas acid mist emissions can be achieved by fiber mist eliminators and electrostatic precipitators (ESPs). Although ESPs are frequently used in the purification section of spent acid plants, there is no evidence that any have been installed to treat the stack gas of any new sulfuric acid plants. Even though ESPs do have the advantage of operating with a lower pressure drop than fiber mist eliminators (normally less than 1 inch of H_2O), lack of application of this equipment to new sulfuric acid units is probably due primarily to its relatively large size and resultant high installation cost compared to fiber mist eliminators and to the high maintenance cost required to keep the ESPs operating

within proper tolerances in the acid environment which is corrosive to the mild steel equipment.

Fiber mist eliminators utilize the mechanisms of impaction and interception to capture large to intermediate size acid mist particles and of Brownian movement to effectively collect micron to submicron size particles. Fibers used may be chemically resistant glass or fluorocarbon. Fiber mist eliminators are available in three different configurations covering a range of efficiencies required for various plants having low to high acid mist loadings and coarse to fine mist particle sizes, respectively. The three fiber mist eliminator configurations are:

1. Vertical tube
2. Vertical panels
3. Horizontal dual pads.

4.5.1 Vertical Tube Mist Eliminators

Tubular mist eliminators consist of a number of vertically oriented tubular fiber elements installed in parallel in the top of the absorber on new acid plants and usually installed in a separate tank above or beside the absorber on existing plants. Each element consists of glass fibers packed between two concentric 316 stainless steel screens. In an absorber installation (see Figure 4-10) the bottom end cover of the element is equipped with a liquid seal pot to prevent gas bypassing. A pool of acid provides the seal in the separate tank design. Mist particles collected on the surface of the

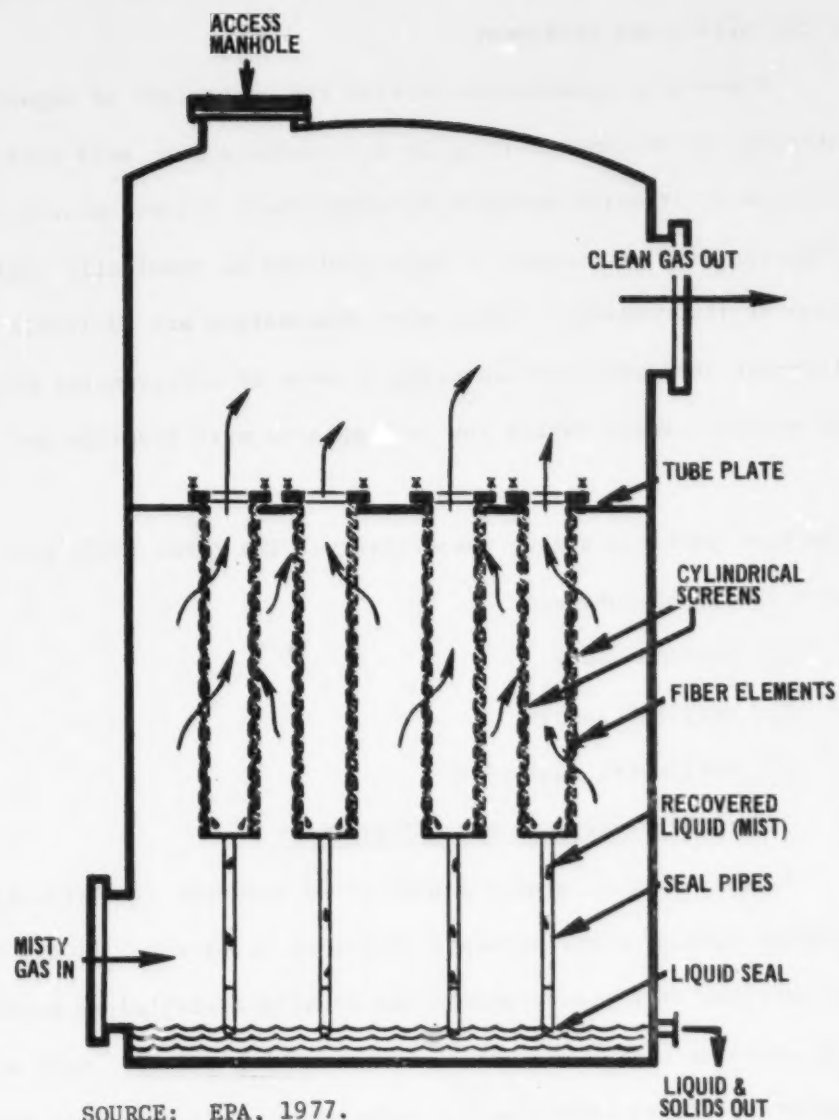


FIGURE 4-10
VERTICAL TUBE MIST ELIMINATOR INSTALLATION

fibers become a part of the liquid film which wets the fibers. The liquid film is moved horizontally through the fiber beds by the gas drag and is moved downward by gravity. The liquid overflows the seal pot continuously, returning to the process.

Tubular mist eliminators use inertial impaction to collect larger particles (normally greater than 3 microns) and use direct interception and Brownian movement to collect smaller particles. The low superficial velocity of gas passing through the fiber bed--6 to 12 meters/minute--provides sufficient residence time for nearly all of the small particles with random Brownian movement to contact the wet fibers, effecting removal from the gas stream. The probability that such a particle could pass through the bed following the resultant greatly lengthened travel path is very low.

Design volumetric flow rate through an element is about 28.3 sm³/min, and the number of elements required for a given plant size can be determined from the standard cubic meters per minute handled at capacity. Depending on the size of the sulfuric acid plant, anywhere from 10 to 100 elements may be used; each element is normally 0.6 meters in diameter and 3 meters high.

Pressure drop across the element varies from 13 to 38 cm. of H₂O with a higher pressure drop required for a higher removal efficiency on particles smaller than 3 microns. The manufacturer of these elements guarantees a mist removal efficiency of 100 percent on particles larger than 3 microns and 90 to 99.8 percent on particles

smaller than 3 microns with 99.3 percent being most common. These efficiencies can be achieved on the stack gas of sulfuric acid plants burning elemental sulfur or bound-sulfur feedstocks (spent acid, wet gas, etc.) and producing acid or oleum.

Because the vertical tube mist eliminator does not depend only upon impaction for mist removal, it can be turned down (operated at a volumetric flow rate considerably below design) with no loss in efficiency.

Available information indicates that the vertical tube mist eliminator is used in the great majority of new sulfuric acid units for acid mist control.

4.5.2 Vertical Panel Mist Eliminators

Panel mist eliminators use fiber panel elements mounted in a polygon framework closed at the bottom by a slightly conical drain pan equipped with an acid seal pot to prevent gas bypassing. The polygon top is surmounted by a circular ring which is usually installed in the absorption tower and welded to the inside of the absorption tower head. Each panel element consists of glass fibers packed between two flat parallel 316 stainless steel screens. In large high velocity towers, recent designs have incorporated double polygons, one inside the other, to obtain more bed area in a given tower cross section.

As in the high efficiency tubular mist eliminator above, the gas flows horizontally through the bed, but at a much higher superficial

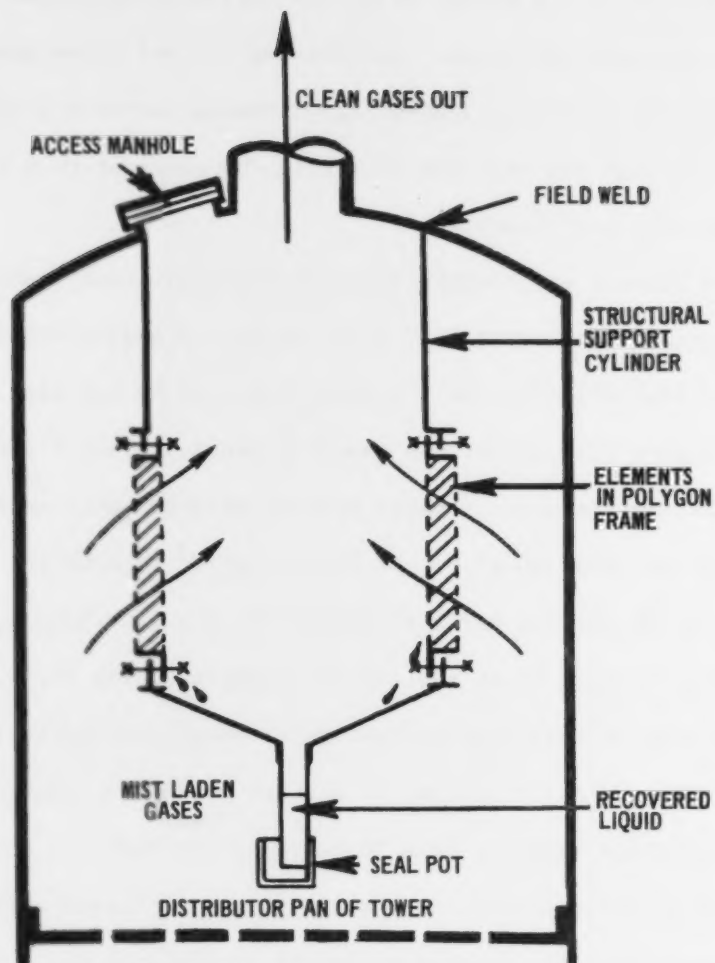
velocity (120 to 150 m/min) using the impaction mechanism for collection of the mist particles. Gas leaving the bed flows upward to the exit port, while the collected liquid drains downward across the pan and out through the seal pot back into the tower or to a separate drain system (see Figure 4-11).

The polygon may contain 10 to 48 vertical sides, each side normally consisting of an 18 1/2" x 53" panel. A smaller 18 1/2" x 26" panel is available for small plants, e.g., 32 Mg per day.

Pressure drop across the panel is usually about 8 inches of H₂O. The manufacturer of panel mist eliminators will usually guarantee an emission no higher than 2 mg/ft³ (equivalent to 0.375 lb/ton of 100 percent H₂SO₄ produced) for a sulfur-burning plant producing oleum up to 20 percent in strength and/or acid.

Because of the large percentage of submicron (below 1 micron) mist present in the stack gas of a spent acid plant and of a plant producing oleum stronger than 20 percent, the vertical panel mist eliminator will usually give unsatisfactory performance for these plants when used for acid mist control in the tail gas. These units find application in new dual absorption plants for acid mist removal from the intermediate absorber in order to afford corrosion protection for downstream equipment.

Vertical panel mist eliminators normally operate with a liquid level in the acid seal pot below the conical drain pan. Although the velocity through the panels could be increased at lower throughputs



SOURCE: EPA, 1977.

FIGURE 4-11
VERTICAL PANEL MIST ELIMINATOR INSTALLATION

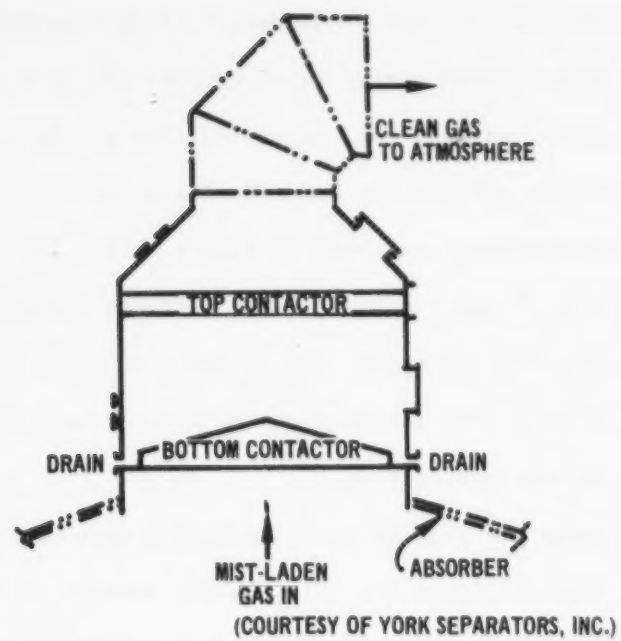
by raising the liquid level to cover the lower part of each panel, this would not be good practice since it would cause reentrainment of spray by the gas passing over the liquid level in the basket.

4.5.3 Horizontal Dual Pad Mist Eliminators

Two circular fluorocarbon fiber beds held by stainless steel screens are oriented horizontally in a vertical cylindrical vessel one above the other, so that the coarse fraction of the acid mist is removed by the first pad (bottom contactor) and the fine fraction by the other (top contactor), as shown in Figure 4-12. The bottom contactor consists of two plane segmented sections installed at an angle to the horizontal to facilitate drainage and give additional area for gas contact. The assembly may be located adjacent to--or positioned on--an absorption tower.

This unit uses the high velocity impaction mist collection mechanism, as does the panel mist eliminator; however, the collected acid drains downward through the pads countercurrent to the gas flow producing a scrubbing action as well. Collected acid may be drained from external connections or returned directly to the absorber through liquid seal traps.

Total pressure drop across both pads is usually about 23 cm. of H_2O . The superficial velocity through the unit is 2.7 to 3.0 m/s. Hence, the diameter of the cylindrical shell and the pads is determined from the volume of gas handled. Height requirements for the unit depend upon whether it is located adjacent to or positioned on



SOURCE: EPA, 1977.

FIGURE 4-12
HORIZONTAL DUAL PAD MIST ELIMINATOR

the absorber, but are roughly 1.5 to 2 times the diameter of the unit.

As with the panel mist eliminator, the dual pad unit will reduce acid mist emissions to 2 mg/ft^3 (0.375 lb/ton of 100 percent H_2SO_4) or less, provided the plant burns sulfur and does not produce oleum stronger than 20 percent, and provided that a particle size distribution curve shows that this level can be met.

5.0 INDICATIONS FROM NSPS COMPLIANCE TEST RESULTS

5.1 Test Results from EPA Regional Sources

The Metrek Division of The MITRE Corporation conducted a survey of all 10 EPA regions to gather available NSPS compliance test data for each of the 10 industries under review (MITRE Corporation, 1978). This survey yielded test data on 20 new sulfuric acid units. Data included average SO₂ and acid mist emissions and 100 percent sulfuric acid production rates for these units. In all cases, the sulfuric acid production rate was at the unit design maximum (the actual production rates usually exceeded the nominal design rates by 5 to 10 percent). Only a few values of opacity readings were reported as compared with the total number of tests.

Telephone contacts with EPA regional personnel and, in some cases, with sulfuric acid plant operators yielded NSPS compliance test data on an additional 12 new sulfuric acid units. In all, 29 sets of data were obtained representing 32 new sulfuric acid units (in two cases, the NSPS tests were run on two or more new units combined). Insofar as is known, the test data obtained represent all of the sulfuric acid units completed from 1971 through 1977, and subject to NSPS.

5.2 Analysis of NSPS Test Results

The results of the NSPS compliance tests for the 32 new sulfuric acid units are tabulated in Table 5-1 and displayed in Figures 5-1 and 5-2 for SO₂ and acid mist emissions, respectively. Table 5-2

TABLE 3-1
HAPS COMPLIANCE TEST RESULTS FOR SULFURIC ACID PLANTS

EPA Region	Company	Plant Location	Stack Output Rate (100% H ₂ SO ₄) kg/day/TPD	Average SO ₂ Emissions kg/hr of 100% H ₂ SO ₄ (lb/hr)	Average Acid Mist Emissions kg/hr of 100% H ₂ SO ₄ (lb/hr)	Actual Plant Product Rate During HAPS Test kg/day 100% H ₂ SO ₄ (tpd)	Measured Opacity During Test (percent)	Reference
II	RL Industries, Inc.	Rayville, N.J.	910 (1000) 910 (1000)	0.71 (1.42) 1.9 (3.7)	0.018 (0.033) 0.082 (0.123)	843 (929) 800 (880)	0 0	Wigley et al., 1975 1975
IV	Agripco Chemical, Inc. CF Chemicals, Inc. CF Chemicals, Inc.	San Pierce, Fla. Bartow, Fla. Plant City, Fla.	1440 (1600) 1600 (1000) 1440 (1600)	1.11 (2.23) 0.96 (1.12) 0.76 (1.33)	0.055 (0.109) 0.010 (0.021) 0.036 (0.116)	1679 (1790) 1791 (1957) 1562 (1717)		CBS, 1976 CBS, 1976 CBS, 1976
	Cardinal, Inc.	Tampa, Fla.	1440 (1600)	1.26 (2.52)	0.056 (0.052)	1277 (1403)	0-5	Garrett, 1978
	M.R. Grace Co.	Bartow, Fla.	1440 (1600)	0.87 (1.73)	0.036 (0.071)	2426 (2664)	0-5	Garrett, 1978
	IMC Chemical Corp.	Mulberry, Fla.	1440 (1600)	0.16 (0.32)	0.039 (0.083)	1616 (1716)		CBS, 1978
	Oxidant Petroleum Corp.	White Springs, Fla.	1440 (1600)	1.05 (2.10)	0.02 (0.04)	1347 (1400)		Wu, 1978
	Am. Cyanamid Co.	Savannah, Ga.	1440 (1600)	1.2 (2.3)	0.07 (0.13)	1333 (1487)		Wu, 1978
	Mislanip Chemical Corp.	White Springs, Fla.	1440 (1600)	0.73 (1.43)	0.008 (0.016)	2657 (2760)		CBS, 1978
	Trusagulf, Inc.	Leo Creek, N.C.	1370 (1500)	0.45 (1.30)	0.011 (0.022)	2366 (2600)		CBS, 1978
			1370 (1500)	1.62 (3.23)	0.071 (0.142)	2303 (2700)		CBS, 1978
				0.47 (0.93)	0.064 (0.127)	1641 (1803)		CBS, 1978
				1.17 (2.33)	0.030 (0.059)	779 (856)		Garrett, 1978
V	Aslin Corp. ^a	Wood River, Ill.	230 (250)	1.85 (3.69)	0.072 (0.144)	219 (241)		Cohen, 1978
VI	Agripco Chemical, Inc. Agripco Chemical, Inc. Freemont Chemical Co. Bolin & Nease, Inc.	Dandaleville, La. Covington, La. Boer Park, Va.	1440 (1600) 1440 (1600) 1440 (1600)	0.55 (1.10) 0.55 (1.11) 1.0 (1.99)	0.037 (0.073) 0.042 (0.085) 0.08 (0.15)	1836 (2011) 1677 (1843) 1694 (1862)	<10 <10	Chubb, 1978 Stonk, 1978 Speidel, 1978
IX	Valley Nitrogen Producers, Inc.	Wahala, Calif.	1440 (1600)	1.16 (2.32)	0.041 (0.082)	716 (787)	9.2	Speidel, 1978
X	Baker Industries, Inc. J.R. Hagler Co. Allied Chemical Corp.	Cando, Idaho Pocatello, Idaho Amesbury, Mass.	770 (810) 810 (900) 300 (330)	1.36 (3.02) 0.53 (1.05) 1.70 (3.41) ^c	0.053 (0.105) 0.046 (0.092) ^b 0.04 (0.075) ^c	1201 (1100) 853 (936) ^b 222 (244)	<3 3	Reynolds, 1978 Pfander, 1978 Pfander, 1978 Tomson & Hayward, 1976

^aThis facility was purchased by Shell Oil Co. in 1976; the plant is being modified to incorporate a double absorption process for SO₂ control.

^bLocal output of two units.

^cAverage of three units.

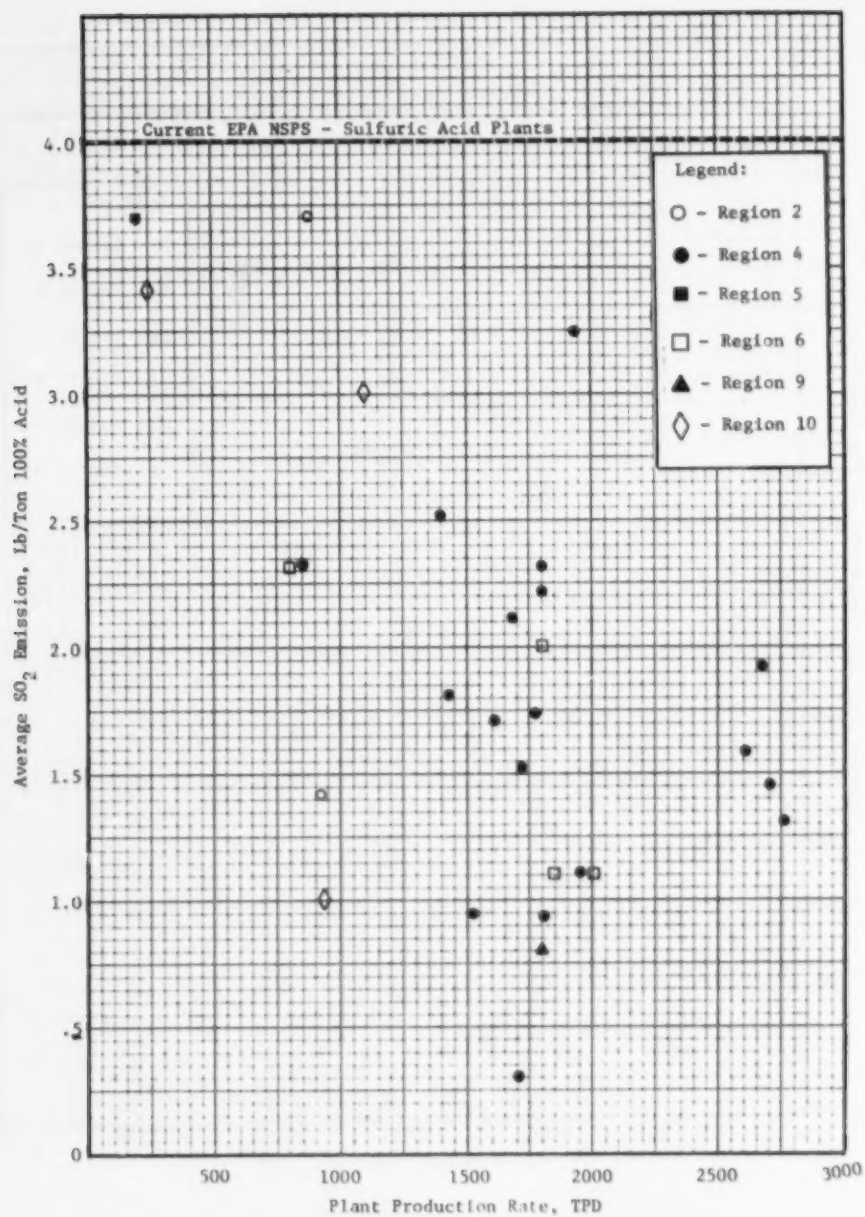


FIGURE 5-1
CONTACT PROCESS SULFURIC ACID PLANTS
NSPS COMPLIANCE TEST RESULTS
SO₂ EMISSIONS

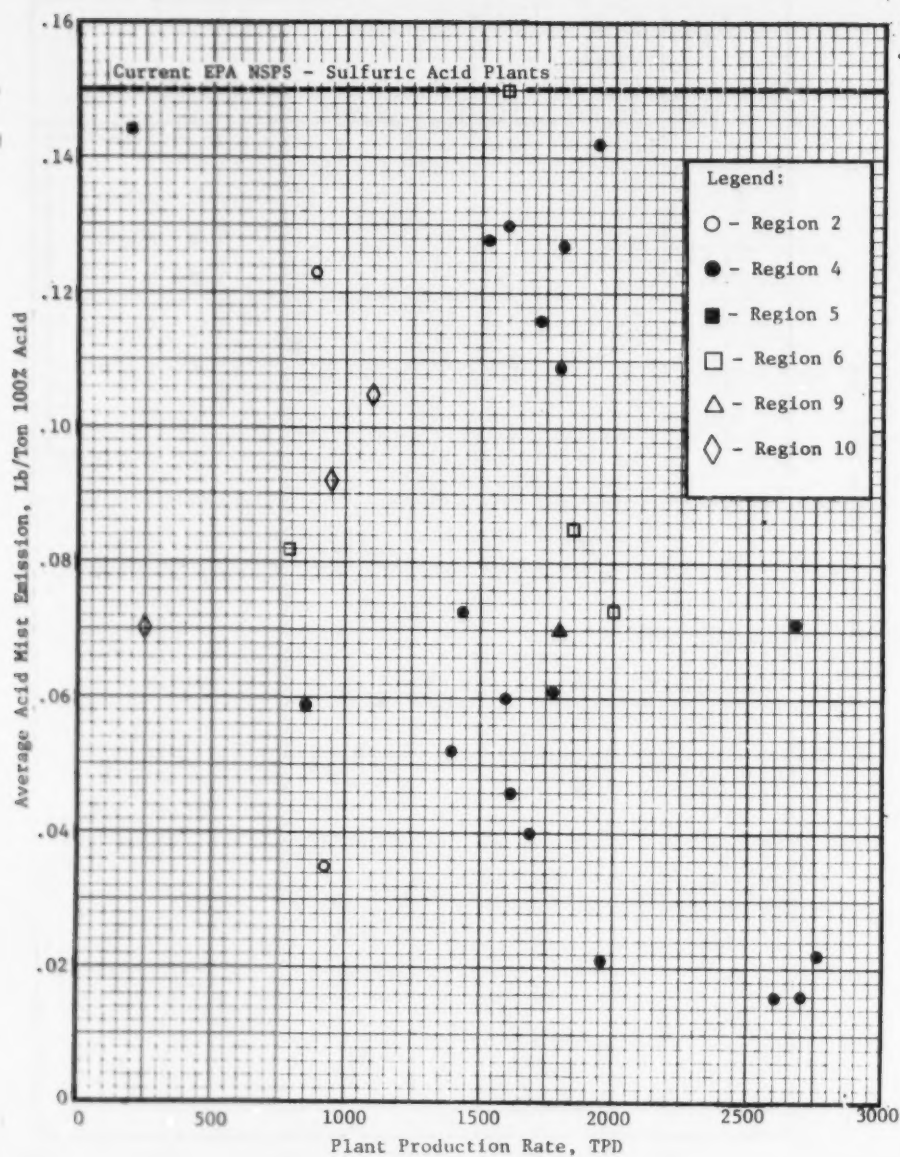


FIGURE 5-2
CONTACT PROCESS SULFURIC ACID PLANTS
NSPS COMPLIANCE TEST RESULTS
ACID MIST EMISSIONS

TABLE 5-2

NSPS COMPLIANCE TEST RESULTS
FOR NEW SULFURIC ACID PLANTS
BREAKDOWN BY EMISSIONS LEVEL

SO ₂			Acid Mist		
NSPS Test Results (lb/ton)	No. of Results	% of Total	NSPS Test Results (lb/ton)	No. of Results	% of Total
3.0 to 4.0	5	17	0.13 to 0.15	3	10
2.0 to 3.0	6	21	0.11 to 0.13	5	17
1.0 to 2.0	14	48	0.09 to 0.11	2	7
0 to 1.0	4	14	0.07 to 0.09	6	21
	29	100	0.05 to 0.07	6	21
			0.03 to 0.05	3	10
			0.01 to 0.03	4	14
				29	100

presents a percentage breakdown of NSPS SO₂ and acid mist emission results at various levels below the respective control levels.

5.2.1 Control Technology Used to Achieve Compliance

All 32 units tested showed compliance with the NSPS SO₂ and acid mist control levels. Of the 32 units tested, 28 achieved compliance with the SO₂ standard through use of the dual absorption process. Of the remaining four units, three use ammonia scrubbing and one employs a molecular sieve process* to meet the standard. All of the new units use mist eliminators to achieve acid mist control. The bulk of these control units are vertical tube mist eliminators. Only nine values of opacity were reported (all meeting the NSPS standard). It is assumed that all of the new plants were meeting the opacity standard during the compliance tests since opacity is directly related to acid mist concentration.

In one vendor's modification of the dual absorption process (the R.M. Parsons Co., Pasadena, California), the usual four-bed catalytic converter was replaced with a five-bed unit, i.e., three beds are used for SO₂ conversion prior to the interpass or primary absorption tower, followed by two beds being utilized for further SO₂ conversion before the final absorber. This method is intended to achieve 99.8 to 99.9 percent conversion to SO₃ equivalent to approximately 0.5 kg/Mg (1.0 lb/ton) SO₂ emission level in the tail gas. Eight new dual absorption units incorporating this design have

*Due to operational difficulties, the molecular sieve operation is currently being replaced by a dual absorption plant.

been installed (Field, 1978). The Parsons units are identified in Table 4-5. Inspection of Table 5-1 indicates that the Parsons units show a range of SO₂ emissions from 0.4 kg/Mg (0.8 lb/ton) to 1.7 kg/Mg (3.4 lb/ton), with the average being approximately 1.0 kg/Mg (2.0 lb/ton). Based on NSPS compliance test results, it appears that the SO₂ emission levels obtained from these five-bed units have not been able to reach the original design levels.

5.2.2 Statistical Analysis of NSPS Compliance Test Data

The arithmetic mean and 95 percent confidence interval has been calculated for the dual absorption plant NSPS test results. The arithmetic mean for SO₂ is 0.9 kg/Mg (1.8 lb/ton) with a 95 percent confidence interval of ± 0.15 kg/Mg (± 0.3 lb/ton). The arithmetic mean for acid mist emissions is 0.04 kg/Mg (0.08 lb/ton) with a 95 percent confidence interval of ± 0.01 kg/Mg (± 0.02 lb/ton). The wider 95 percent confidence limits for acid mist emissions are indicative of a greater spread in acid mist emission results (as can be seen by comparing Figures 5-1 and 5-2).

5.2.3 Validity of NSPS Test Data

The 26 data points obtained for dual absorption plants equipped with high efficiency acid mist eliminators show a rather large spread for SO₂ control levels, i.e., SO₂ emission values range from a low of 0.16 kg/Mg (0.32 lb/ton) to a high of 1.9 kg/Mg (3.7 lb/ton). Additionally, the corresponding acid mist emission values range from a low of 0.008 kg/Mg (0.016 lb/ton) to a high of 0.071 kg/Mg (0.14 lb/ton). All data were obtained using the standard EPA Method 8.

It is not clear why the use of this test method should have produced such a wide variation in the test results for plants with identical control technologies. Region IV believes that at least part of the observed variation may be due to differences in test contractor's techniques (Rom, 1978). In this regard, discussion with EPA personnel in the Quality Assurance Branch (QAB) of the Environmental Monitoring and Support Laboratory indicate areas where the original Method 8* (used in testing all of new sulfuric acid units subject to NSPS) could yield misleading SO₂ and acid mist results. Detailed studies of the original Method 8 by QAB indicated that the isopropanol (IPA) used in the test could contain trace quantities of peroxide, which, if present, would react with SO₂ during the test procedure to form SO₃, yielding lower SO₂ and higher acid mist values in the tail gas. Additionally, when the test contractor performed the impinger train leak check, upon release of the applied vacuum, a fine spray of hydrogen peroxide solution could deposit on the filter, causing the SO₂ → SO₃ conversion mechanism to be set into motion during the tail gas sampling period. This again could result in misleading levels of SO₂ and acid mist in the tail gas (Midgett, 1978).

The revised Method 8 has attempted to remedy these defects in the original test.* This method requires that the IPA be tested for

*Method 8 was revised effective August 18, 1977.

peroxides. If the latter are found, the IPA batch must either be discarded or treated to remove the peroxide. Since operator technique is the controlling factor in minimizing errors due to the leak check, the revised Method 8 provides a warning to the test equipment operator to avoid this pitfall by careful manipulation of the equipment.

In summary, it would seem reasonable to have some question about the validity of the SO₂ and acid mist results obtained from the NSPS compliance tests made prior to August 1977 on the grounds of the reliability of the test method itself.

5.2.4 Comparison of NSPS Compliance Test Data with Day-to-Day Emission Control Performance

MITRE has made a number of inquiries of sulfuric acid plants that are operating units subject to NSPS to ascertain whether the compliance test data for these units represent the current day-to-day emission control levels. A literature search had indicated that NSPS emission controlled plants (dual absorption) could be expected to operate (after an initial startup period with fresh catalyst) with SO₂ emissions in the 1 to 1.5 kg/Mg (2 to 3 lb/ton) range. One recent literature reference indicated that a new sulfuric acid unit with an NSPS SO₂ test value of 0.56 kg/Mg (1.12 lb/ton) in 1975, was currently averaging 1.5 kg/Mg (3.0 lb/ton) SO₂ emissions (PEDCo, 1977). Another reference indicated that a typical dual absorption plant with an average SO₂ NSPS compliance test result of 0.85 kg/Mg (1.70 lb/ton) was operating at an average SO₂ emission level of 1.15 kg/Mg (2.3 lb/ton) (EPA, 1976).

Data obtained from one new dual absorption sulfuric acid unit points up the effect of plant and catalyst aging on the SO₂ emission level. These data are tabulated in Table 5-3.

TABLE 5-3

EFFECT OF PLANT AND CATALYST AGE ON SO₂ EMISSION LEVEL^a

Date	Source of Data	SO ₂ Emissions kg/Mg (lb/ton)
9/17/75	NSPS Compliance Test (EPA Method 8)	0.47 (0.93)
10/22/76	Dupont Continuous SO ₂ Monitor ^b	1.30 (2.59)
4/4/77	Dupont Continuous SO ₂ Monitor ^b	1.43 (2.85)
3/28/78	Dupont Continuous SO ₂ Monitor ^b	1.6 (3.2)

^aThis is an 1800 ton/day (100 percent H₂SO₄) plant.

^bResults of Dupont continuous monitor checked concentrations, when converted to kg/Mg of 100 percent acid, checked to within 1 percent of EPA Method 8.

Source: Mullins, 1978.

This plant (a total of two units subject to NSPS) is stated to operate at an SO₂ emission level of 1.25 to 1.50 kg/Mg (2.5 to 3.0 lb/ton) on a day-to-day basis (Mullins, 1978).

Another plant which had an SO₂ NSPS test result of 0.48 kg/Mg (0.95 lb/ton) indicated that this result was obtained with fresh catalyst and that the day-to-day operating value of SO₂ emissions averaged 0.5 to 1.0 kg/Mg (1 to 2 lb/ton) (Stark, 1978).

In summary, indications from the literature and from contacts with sulfuric acid plant operators are that low NSPS compliance test

SO₂ emission values do not necessarily reflect day-to-day plant operating levels. These levels appear to realistically lie in the 1 to 1.5 kg/Mg (2 to 3 lb/ton) range for dual absorption units. There is a definite trend towards increased SO₂ emission values as the conversion catalyst ages and its activity correspondingly decreases. Thus, even though a large percentage of the compliance test results are significantly less than the NSPS of 2 kg/Mg (4 lb/ton), it appears that SO₂ emissions tend to rise towards the control limit as the plant and catalyst age.

Acid mist emission (and related opacity) levels are unaffected by conversion catalyst aging, being primarily a function of moisture levels in the sulfur feedstock and air fed to the sulfur burner, and the efficiency of final absorber operation. The wide spread observed in NSPS compliance test values is probably a result of variations in these factors or quite possibly errors in the test method itself (as discussed in Section 5.2.3).

5.2.5 Emission Control Performance Based on Excess Emissions Reports

It was not possible to evaluate excess emissions reports with regard to sulfuric acid plant SO₂ and acid mist control performance, since a very limited number of reports were available.

5.3 Indications of the Need for a Revised Standard

5.3.1 SO₂ Standard

At this time, there is not sufficient justification for revision of the present SO₂ NSPS, based on the following considerations:

- The current best demonstrated control technology (the dual absorption process) is identical in basic design to that used as the rationale for the original SO₂ standard.
- While the SO₂ NSPS compliance test data averages close to 1 kg/Mg (2 lb/ton) with a number of values in the 0.5 kg/Mg (1 lb/ton) to 1 kg/Mg (2 lb/ton) range, an analysis of these data indicates that:
 1. There may be some question about the validity of the low values of SO₂ emissions based on defects in the original EPA Method 8.
 2. Actual plant experience shows that the low NSPS values do not necessarily reflect the day-to-day operating SO₂ emission levels which tend to rise toward the standard as the conversion catalyst ages.
- According to a prime manufacturer of dual absorption plants, in order to guarantee performance at the present level, a margin of safety is built into the unit design to compensate for the effects of plant and catalyst aging, fluctuating feed rates and other deviations from ideal operating conditions. Construction of new plants to meet an appreciably lower SO₂ NSPS involves greatly increased capital costs, since a margin of safety would have to be built into the new plant to meet performance guarantees (Donovan et al. 1977).
- A trend toward higher levels of SO₂ in the gas feed to the converter, i.e., 12 percent SO₂ or higher may develop in the industry, since there is appreciable energy savings due to the additional heat recovery available from the highly exothermic conversion reaction. Meeting an SO₂ emission standard appreciably lower than 2 kg/Mg (4 lb/ton) in this situation would be extremely difficult without extensive (and expensive) equipment additions to the plant.

Other considerations, including economic factors, that militate against a change in the present SO₂ NSPS are discussed in Section 6.0.

5.3.2 Acid Mist NSPS (and Related Opacity Standard)

At this time, there is not sufficient justification for revision of the present acid mist (and opacity) NSPS, based on the following considerations:

- The current best demonstrated control technology (the high efficiency acid mist eliminator) is identical to that used as the rationale for the original acid mist standard.
- The NSPS compliance test data showed a wide scatter, with an appreciable number of the acid mist emission values close to the control limit. The scatter observed in these values may be due to the defects in the original EPA Method 8 which tended to introduce variability in the acid mist levels obtained.
- Making the acid mist standard more stringent is not believed to be practicable because of the need to provide a margin of safety due to in-plant operating fluctuations. Variation in the sulfur feedstock, leaks, or improper inlet air drying tower operation can introduce moisture (the controlling factor in the production of acid mist) into the system, increasing the production of acid mist. It should be noted that acid mist control is far more vulnerable to operating fluctuations which deviate from standard plant operating conditions than sulfur dioxide control.
- Manufacturers of acid mist eliminators guarantee maximum stack emission of 1 mg/scf (0.15 lb/ton) for high-efficiency units. These manufacturers do not guarantee any form of visible emission limitation, but acid mist emissions of 1 mg/scf normally result in stack plumes of less than 10 percent opacity (Serne and Weisenberg, 1976).

6.0 ANALYSIS OF POSSIBLE REVISIONS TO THE STANDARD

6.1 Effect of NSPS Revision on Sulfuric Acid Production Economics

The SO₂ emissions in a dual absorption plant are primarily determined by the efficiency of the catalytic converter system. Acid mist emissions are controlled by plant operators' attention to control of residual moisture in the SO₂-laden inlet gas to the system and to efficient absorber and acid mist eliminator operation. NSPS compliance test values of these emissions, which are appreciably below the present control levels, are, as has been shown in Sections 5.2 and 5.3, not necessarily representative of the levels achievable by a particular plant on a day-to-day basis. Additional capital and/or operating expense would be entailed by plants using the present best demonstrated control technology in order to reduce NSPS control levels appreciably below the present values.

Additional capital expense required to control emissions below the present NSPS levels would be involved for a scrubber installation to further reduce SO₂ in the tail gas from the dual absorption system or an additional acid mist eliminator in series with the present unit to further reduce acid mist.

As shown in Section 5.0, NSPS SO₂ levels for new plants tested predominantly in the 1 to 1.25 kg/Mg (2 to 2.5 lb/ton) range. Making the standard more stringent in order to accomplish reduction of SO₂ emissions appreciably below the present NSPS control level on a day-to-day basis, can probably be achieved by increasing sulfuric acid

plant operating expense significantly. Since SO_2 emissions are directly affected by the level of catalyst activity, the former should be able to be maintained at levels comparable to the observed NSPS compliance test values, if fresh catalyst with the maximum activity were to arbitrarily replace older material in the converter beds at frequent intervals. The economics of a catalyst replacement program have been developed and applied to the cost of producing sulfuric acid in a dual absorption plant, as described below.

In the four-bed catalytic converter system in a typical dual absorption plant, the first bed exposed to the inlet gas experiences the greatest rate of activity decrease due to dirt and traces of catalyst poisons, with beds two and three suffering progressively less loss of activity due to these contaminants. These beds have an average service life of 3 to 5 years. The final catalyst bed, which treats the SO_2 -laden gas from the first absorption tower, can have a service life of 10 to 15 years. Normal plant practice is to progressively elevate these catalyst beds during the plant turnaround periods so that the overall average bed life is 5 to 7 years.

The basic information used in the catalyst replacement cost calculations is summarized in Table 6-1, and the results of the calculations are shown in Table 6-2.

Based on a sulfuric acid manufacturing cost of \$36/Mg, the incremental increase of 55 cents/Mg for the catalyst replacement program outlined above, represents only a 1.4 percent increase. With

TABLE 6-1

BASIC DATA USED IN CATALYST REPLACEMENT COST CALCULATIONS

Items	Source
• 1000 Mg/day dual absorption plant	Design Basis
• 4 Bed Converter	Design Basis
• First three beds (Beds 1, 2 and 3) - Average life of 3-5 years, Final bed (Bed 4) - Average life of 10-15 years	Sheputis, 1978
• Average catalyst makeup rate (first bed) is 10 percent per year due to screening and attrition losses	Sheputis, 1978
• Catalyst loading of 140 liters/daily Mg of acid at 10.5% SO ₂ in inlet gas to converter	Monsanto Enviro-Chem, 1974
• Total catalyst replacement cost is \$3/liter installed	Sheputis, 1978
• Total sulfuric acid manufacturing cost is \$36/Mg (direct and fixed costs)	Hansen, 1978
• Average pretax profit for merchant sulfuric acid is \$3/Mg	EPA, 1977

TABLE 6-2

EFFECT OF CATALYST REPLACEMENT ON COST OF PRODUCTION OF
SULFURIC ACID IN A DUAL ABSORPTION PLANT

ASSUMPTIONS

- In order to maintain overall catalyst activity at a level to obtain SO₂ conversion equivalent to emission of 1 to 1.25 kg/Mg of 100 percent acid (2 to 2.5 lb/ton), replace catalyst beds on the following schedule:
 - Bed 1: Complete replacement once a year (a net replacement of 90 percent of the original bed).
 - Bed 2: Complete replacement once every 2 years.
 - Bed 3: Complete replacement once every 3 years.
 - Bed 4: Complete replacement once every 10 years.
- Each bed holds 25 percent of the total catalyst loading.
- Plant operates 350 days per year.

Bed No.	Annual Catalyst Volume Replaced (liters)	Annual Catalyst Replacement Cost, \$	Mg/Yr of 100% Acid Produced	Annual Catalyst Replacement Cost \$/Mg of Acid Produced
1	31,500	94,500	350,000	0.27
2	17,500	52,500	350,000	0.15
3	11,700	35,100	350,000	0.10
4	3,500	<u>10,500</u>	350,000	<u>0.03</u>
Totals		192,600		0.55

a present FOB plant selling price for 100 percent merchant acid of approximately \$50/Mg (Gulf Coast area) (Chemical Marketing Reporter, 1978), an incremental increase of 55 cents/Mg for catalyst replacement represents only 1 percent of the selling price. However, the effect of this cost on pretax profit, based on an average pretax profit of \$3/Mg, is much more drastic, i.e., 55 cents/Mg for annual catalyst replacement represents an approximate 20 percent reduction in pretax profit. An adverse economic penalty to the sulfuric acid industry would seem to be indicated by this approach.

A serious problem raised by the catalyst replacement program outlined above would be the need to dispose of the highly toxic spent vanadium pentoxide catalyst waste generated. This material is not considered valuable enough to rework by the major processors. Some of the catalyst disposed of at present is reworked by several marginal processors (Sheputis, 1978).

6.2 Effect of New Sulfuric Acid Plant Construction on the NSPS

As mentioned in Section 4.2, the rate of completion of new sulfuric acid units during the 1971-1977 period was approximately 5 per year. During the 1978-1980 period, the number of new sulfuric acid units announced or under construction has slowed to approximately 3 per year. This slowdown in new growth is due primarily to the present imbalance in the demand-supply situation in the phosphate fertilizer industry. Based on anticipated growth in the phosphate fertilizer industry, an estimate for the 1981 to 1984 period of four new sulfuric acid units completed per year has been used as a basis

for calculating the total SO₂ and acid mist emissions at various emission levels for the 16 new units projected to be completed during this period. The results of these calculations are shown in Tables 6-3 and 6-4.

A study of Table 6-3 indicates that reducing the NSPS control level for SO₂ emissions from the present 2 kg/Mg (4 lb/ton) to 1 kg/Mg (2 lb/ton), a 50 percent reduction, would reduce the total SO₂ emissions for sulfuric acid plants regulated by the NSPS by approximately 6000 Mg/yr (7000 tons/yr) in 1984. Correspondingly, a study of Table 6-4 indicates that reduction of the NSPS acid mist control levels from the present 0.075 kg/Mg (0.15 lb/ton) to 0.05 kg/Mg (0.10 lb/ton), a 33 1/3 percent reduction, would reduce the total acid emissions for these sulfuric acid plants by approximately 150 Mg/yr (170 tons/yr) in 1984.

As a further comparison of the potential impact of SO₂ emissions from sulfuric acid units projected to be built between 1981 and 1984, data from projections of SO₂ emissions from all stationary sources in 1984 were used to calculate the effect of sulfuric acid plant SO₂ NSPS reduction. Total SO₂ emissions from stationary sources in 1984 (based on all existing NSPS and state standards in effect in 1975) are indicated to be approximately 33×10^6 Mg/yr (EPA, 1976). With the present sulfuric acid NSPS of 2 kg/Mg (4 lb/ton), the percent SO₂ emission contribution of the projected 16 new units in 1984 would be 0.04 percent. Correspondingly, with an NSPS

TABLE 6-3
PROJECTED CUMULATIVE SO₂ EMISSIONS FROM NEW CONTACT SULFURIC
ACID PLANTS ADDED BETWEEN 1981 AND 1984^a

Control Level kg/Mg (lb/ton)	Projected Emissions Mg/yr (ton/yr) ^b				Percent of Total Annual SO ₂ Emissions of NSPS Plants in 1984 ^c
	1981	1982	1983	1984	
2.0 (4.0)	3,060(3,360)	6,120(6,720)	9,180(10,080)	12,230(13,440)	27.6
1.75 (3.5)	2,680(2,940)	5,350(5,880)	8,030(8,820)	10,700(11,760)	25.0
1.5 (3.0)	2,290(2,520)	4,590(5,040)	6,880(7,560)	9,170(10,080)	22.2
1.25 (2.5)	1,910(2,100)	3,820(4,200)	5,730(6,300)	7,640(8,400)	18.8
1.0 (2.0)	1,530(1,680)	3,060(3,360)	4,590(5,040)	6,120(6,720)	16.0

^aFour contact process double-absorption sulfuric acid plants (average production capacity of 1100 Mg/day (1200 tons/day) of 100% H₂SO₄ each) are projected to be installed per year from 1981-1984, inclusive.

^bCalculations based on a 350-day work year.

^cTotal annual SO₂ emissions of 42 existing NSPS H₂SO₄ units in 1984 (at present 4.0 lb/ton control level) is 33,000 Mg/yr² (35,300 tons/yr).

TABLE 6-4
PROJECTED CUMULATIVE ACID MIST EMISSIONS FROM NEW CONTACT SULFURIC
ACID PLANTS ADDED BETWEEN 1981 and 1984^a

Control Level kg/Mg (lb/ton)	Projected Emissions Mg/yr (ton/yr) ^b				Percent of Total Annual Acid Mist Emissions of NSPS Plants in 1984 ^c
	1982		1983		
	1981	1982	1983	1984	
0.075 (0.15)	115(126)	229(252)	344(378)	459(504)	27.6
0.07 (0.14)	108(119)	217(238)	325(357)	433(476)	26.4
0.065 (0.13)	99(109)	197(217)	297(326)	395(434)	24.7
0.06 (0.12)	93(102)	185(203)	278(305)	369(406)	23.5
0.055 (0.11)	83(91)	166(182)	248(273)	331(364)	21.6
0.05 (0.10)	76(84)	153(168)	229(252)	306(336)	20.3

^aFour contact process double-absorption sulfuric acid plants (average production capacity of 1100 Mg/day (1200 tons/yr) of 100% H₂SO₄ each) are projected to be installed per year from 1981-1984, inclusive.

^bCalculations based on a 350-day work year.

^cTotal annual acid mist emissions of 42 existing NSPS units in 1984 (at present 0.15 lb/ton control level) is 1200 Mg/yr (1325 tons/yr).

of 1 kg/Mg (2 lb/ton), the percent SO₂ emission contribution of the projected 16 new units in 1984 would be 0.02 percent. The national impact of a more stringent SO₂ NSPS would be marginal due to the very small decrease in SO₂ emissions (resulting from a tighter standard) from the sulfuric acid plants projected to be built during the 1981 through 1984 period.

7.0 FINDINGS AND RECOMMENDATIONS

The primary objective of this report has been to assess the need for revision of the existing NSPS for sulfuric acid plants, including review of the SO₂ and acid mist standards. The existing opacity standard is directly related to the acid mist standard and is not reviewed separately. The findings and recommendations developed in these two areas are presented below.

7.1 Findings

7.1.1 SO₂ NSPS

7.1.1.1 Process Emission Control Technology.

- The current best demonstrated control technology, the dual absorption process, is identical in basic design to that used as the rationale for the original SO₂ standard. The dual absorption process is in use in over 90 percent of all sulfuric acid production units installed since the promulgation of the SO₂ NSPS for sulfuric acid plants and will be installed in all new plants built through 1980.
- While the overall average SO₂ emission obtained in the NSPS compliance test results is 0.9 kg/Mg (1.8 lb/ton), the wide range shown in this data, from a low of 0.16 kg/Mg (0.32 lb/ton) to a high of 1.9 kg/Mg (3.7 lb/ton) for dual absorption plants, may be partially due to defects in the original Test Method 8 or to variations in test operator technique. The average SO₂ emission level obtained in the NSPS compliance tests for dual absorption plants is about one order of magnitude lower than the emission level obtained from uncontrolled single absorption plants.
- The dual absorption process, while yielding low NSPS compliance test SO₂ emission levels, can not maintain these levels on a day-to-day basis. The SO₂ emission level is a function of catalyst conversion efficiency which drops as the catalyst ages.

7.1.1.2 Economic Considerations.

- In order to guarantee SO₂ emission control performance at the present NSPS level, vendors of the dual absorption process plants incorporate a sufficient margin of safety in the plant design, consistent with reasonable investment cost, to compensate for the effects of plant and catalyst aging, fluctuating feed rates and other deviations from ideal operating conditions. Making the present SO₂ NSPS more stringent would involve greatly increased capital costs since sulfuric acid plant vendors would have to redesign for lower SO₂ emission rates in order to retain this margin of safety.
- More frequent conversion catalyst replacement (as compared with present practice) in order to maintain a more stringent SO₂ control level than the present standard in sulfuric acid plants subject to NSPS would represent a substantial drop in pretax profits (20 percent or more).
- Projections over the 4-year period, 1981 through 1984, for the 16 new sulfuric acid plants expected to be built during this period indicate that there would be only a 0.02 percent drop in SO₂ emission contribution from these plants to the total U.S. annual SO₂ emissions if the present SO₂ standard were dropped from 2 kg/Mg (4 lb/ton) to 1 kg/Mg (2 lb/ton).

7.1.2 Acid Mist NSPS (and Related Opacity Standard)

- The current best demonstrated control technology, the high efficiency acid mist eliminator, is identical to that used as the rationale for the original acid mist standard. This technology is in use in all sulfuric acid plants built since the promulgation of the acid mist NSPS for sulfuric acid plants.
- While the average acid mist emission obtained in the NSPS compliance test results is 0.04 kg/Mg (0.08 lb/ton), the wide range shown in this data, from a low of 0.008 kg/Mg (0.016 lb/ton) to a high of 0.071 kg/Mg (0.14 lb/ton) for high efficiency acid mist eliminator control, may be partially due to defects in the original EPA Method 8 which tended to introduce variability in the acid mist levels obtained.

- An appreciable number (approximately 25 percent) of the NSPS compliance test results obtained for acid mist emissions are within 75 to 100 percent of the present NSPS acid mist control level. This may be indicative of the vulnerability of sulfuric acid plants to in-plant operating fluctuations such as variation in the sulfur feedstock, leaks, or improper inlet air drying tower operations, all of which introduce moisture (the controlling factor in the formation of acid mist) into the system, thus increasing the acid mist emissions.
- Manufacturers of acid mist eliminators guarantee maximum stack emissions of 1 mg/scf (~0.15 lb/ton) for high efficiency units under normal operating conditions. While there is a 10-percent opacity limitation for stack plumes under the present NSPS, no guarantee is provided for any form of visible emission limitation. However, available data indicate that acid mist emissions of 1 mg/scf will result in stack plumes of less than 10 percent opacity.

7.2 Recommendations

7.2.1 SO₂ NSPS

At this time there is not sufficient justification for revision of the SO₂ NSPS for sulfuric acid plants, based on the following considerations:

- The best demonstrated control technology, the dual absorption process, is in use in all new sulfuric acid plants.
- SO₂ emission levels achieved in the NSPS compliance tests which were significantly lower than the standard are not representative of day-to-day plant operations. These levels tend to rise toward the standard as the conversion catalyst ages. The dual absorption process can not adjust the SO₂ emission levels to compensate for the loss of catalyst activity.
- The national impact of a more stringent SO₂ NSPS would be marginal due to the very small decrease in SO₂ emissions (resulting from a tighter standard) from the sulfuric acid plants projected to be built during the 1981 through 1989 period.

7.2.2 Acid Mist NSPS (and Related Opacity Standard)

At this time there is not sufficient justification for revision of the acid mist (and opacity) NSPS based on the following considerations:

- The best demonstrated control technology (the high efficiency acid mist eliminator) is in use in all new sulfuric acid plants.
- The need exists to retain a margin of safety for maintenance of the present acid mist NSPS control level since there is always a possibility of in-plant operating fluctuations which deviate from standard sulfuric acid plant operations and introduce unexpected amounts of moisture into the system.
- Control of acid mist emissions at the present NSPS level, results in essentially no visible emissions, i.e., less than 10 percent opacity.

8.0 REFERENCES

Calvin, E.L. and F. D. Kodras, 1976. Inspection Manual for the Enforcement of New Source Performance Standards as Applied to Contact Catalyst Sulfuric Acid Plants. Catalytic, Inc., Charlotte, N.C.

CE Construction Alert, 1977. Chemical Engineering, Vol. 84, No.6.

Chemical and Engineering News, 1978. Facts and Figures for the Chemical Industry. Vol. 56, No. 24.

Cohen, E., 1978. Personal Communication. EPA Region V, Chicago, Ill.

Donovan, J. R. et al., 1977. Analysis and Control of Sulfuric Acid Plant Emissions, Chemical Engineering Progress, Vol. 73, No. 6.

Duros, D.R. and E.D. Kennedy, 1978. Acid Mist Control. Chemical Engineering Progress, Vol. 74, No. 9, 1978.

Field, D., 1978. Personal Communication. R. M. Parsons Company, Pasadena, Calif.

Gardner, R., 1978. Personal Communication. Georgia Department of Natural Resources, Atlanta, Ga.

Garrett, W., 1978. Personal Communication. Florida Department of Environmental Regulation, Winterhaven, Fla.

Hansen, D. R., 1978. Personal Communication. Monsanto Enviro-Chemical, St. Louis, Mo.

Hooper, M. H., 1978. Personal Communication. EPA Region X, Seattle, Wash.

Mann, C., 1978. Personal Communication. Requests and Information Section, National Air Data Branch, U.S. Environmental Protection Agency, Research Triangle Park, N.C.

Midgett, M. R., 1978. Personal Communication. Quality Assurance Branch, National Air Data Branch, U.S. Environmental Protection Agency, Research Triangle Park, N.C.

Mistry, M. T. et al., 1975. Personal Communication to EPA Region II. Betz Environmental Engineers, Newark, N.J.

MITRE Corporation, 1978. Regional Views on NSPS for Selected Categories. Metrek Division, McLean, Va.

Monsanto Enviro-Chemical, 1974. Vanadium Catalysts for Contact Sulfuric Acid Plants. St. Louis, Mo.

Mullins, F., 1978. Personal Communication. Occidental Petroleum Corporation, White Springs, Fla.

PEDCo Environmental Inc., 1977. Summary Report on SO₂ Control Systems for Industrial Combustion and Process Sources, Vol. IV Sulfuric Acid Plants. Cincinnati, Ohio.

Reynolds, W., 1977. Personal Communication to EPA Region IX, Valley Nitrogen Producers, Inc., Helm, Calif.

Pfander, J., 1978. Personal Communication. EPA Region X, Boise, Idaho.

Rom, J., 1978. Personal Communication. EPA Region IV, Atlanta, Ga.

Serne, J. C. and I. J. Weinsenberg, 1976. Engineering Evaluation of Cities Service Smelter, Copperhill Tennessee for SO₂ Emission Control. Pacific Environmental Services, Inc., Santa Monica, Calif.

Sheputis, J., 1978. Personal Communication. Monsanto Environ-Chemical, St. Louis, Mo.

Shonk, R. D., 1978. Personal Communication. Agrico Chemical Co., Donaldsonville, La.

Snowden, W. D. and D. A. Alguard, 1976. Personal Communication to EPA Region X, Alsid, Snowden & Assoc., Bellevue, Wash.

Spruiell, S., 1978. Personal Communication. EPA Region VI, Dallas, Tex.

Stanford Research Institute, 1977. Directory of Chemical Producers, Palo Alto, Calif.

Stark, C., 1978. Personal Communication. Mississippi Chemical Corporation, Yazoo City, Miss.

U.S. Department of Commerce, 1976. Sulfuric Acid 1976, Current Industrial Reports. M28A(76)-14 Supplement 1. Bureau of the Census, Washington, D.C.

U.S. Department of Commerce, 1977. Sulfuric Acid 1977 Current Industrial Reports. M28A(77)-14 Supplement 1. Bureau of the Census, Washington, D.C.

U.S. Department of the Interior, Bureau of Mines, 1975. Minerals Yearbook 1975, Metals, Minerals, and Fuels. Vol. 1. U.S. Department of the Interior, Washington, D.C.

U.S. Department of the Interior, Bureau of Mines, 1978. Mineral Industry Surveys. U.S. Department of the Interior, Washington, D.C.

U.S. Environmental Protection Agency, 1971. Background Information for Proposed New Source Performance Standards. Office of Air Programs, Research Triangle Park, N.C.

U.S. Environmental Protection Agency, 1971a. Control of Air Pollution from Sulfuric Acid Plants. Emission Standards and Engineering Division, Durham, N.C.

U.S. Environmental Protection Agency, 1976. Sulfuric Acid Plant Emissions During Start-up, Shutdown, and Malfunctions. EPA-600/2-76-010. Industrial Environmental Research Laboratory, Research Triangle Park, N.C.

U.S. Environmental Protection Agency, 1977. Final Guideline Document: Control of Sulfuric Acid Mist Emissions from Existing Sulfuric Acid Production Units. EPA-450/2-77-019. Office of Air Quality Planning and Standards, Research Triangle Park, N.C.

U.S. Environmental Protection Agency, 1976. Priorities and Procedures for Development of Standards of Performance for New Stationary Sources of Atmospheric Emissions. EPA-450/3-76-020. Office of Air Quality Planning and Standards. Research Triangle Park, N.C.

U.S. Environmental Protection Agency, 1978. Compliance Data System Source Data Reports.

Williams, A. R., 1977. Personal Communication to EPA Region V, Shell Oil Company, Wood River, Ill.

Wu, J., 1978. Personal Communication. EPA Region IV, Atlanta, Ga.